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OCTOCHLOROINDIGO AND SOME DERIVATIVES OF TETRACHLOROANTHRANILIC AND TETRACHLOROPHTHALIC ACIDS

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Tetrachloroanthranilic Acid

Tetrachloroanthranilic acid was first made by Tust,[1] who converted tetrachlorophthalic acid into tetrachlorobenzoic acid, nitrated this and then reduced the nitro compound. A much better method for making this acid is the one given by Graebe and Rostovzeff.[2] These authors found, while making an investigation of Hofmann's reaction, that tetrachlorophthalimide could be converted into tetrachloroanthranilic acid practically quantitatively by means of sodium hypochlorite in alkaline solution. Hofmann's reaction was again used by Villiger and Blangey,[3] who worked out the details of the most convenient method for the preparation of tetrachloroanthranilic acid that we have at present. They made the ammonium salt of tetrachlorophthalamic acid by dissolving tetrachlorophthalic anhydride in aqueous ammonia, precipitating the free tetrachlorophthalamic acid by adding a

[1] Ber. d. chem. Ges., **20**, 2441 (1887); **21**, 1533 (1888).
[2] *Ibid.*, **35**, 2748 (1902).
[3] *Ibid.*, **42**, 3550 (1909).

mineral acid and converting this into tetrachloroanthranilic acid by means of sodium hypochlorite in alkaline solution.

The directions of Villiger and Blangey were followed in making the crude tetrachloroanthranilic acid used in this investigation. Pure tetrachlorophthalic anhydride and a standardized alkaline hypochlorite solution are required. The pure tetrachlorophthalic acid used was obtained from the commercial product by the method described by Delbridge[1] and converted into the anhydride by heating for several days at 105°. The purity of this anhydride was checked by making determinations of its molecular weight.[2] A weighed portion of the anhydride was dissolved in tenth normal sodium hydroxide, using ten per cent. excess. On heating, solution took place rapidly and was complete after a few minutes' boiling. A few drops of a solution of phenoltetrachlorophthalein were added as the indicator and about 0.5 cc. excess of tenth normal hydrochloric acid. The solution was then boiled to expel carbon dioxide, cooled, and the excess of hydrochloric acid titrated with sodium hydroxide.

Substance Gram	Tenth normal sodium hydroxide cc.	Molecular weight
0.2808	19.63	286.1
0.3152	22.04	286.0
	Calculated for $C_8O_3Cl_4$,	285.8

The alkaline hypochlorite solution should contain two molecules of sodium hydroxide to one molecule of sodium hypochlorite. In the preparation of this solution, chlorine is passed into a ten per cent. solution of sodium hydroxide as rapidly as complete absorption will allow. The solution is kept at a temperature of about 5° by means of a freezing mixture and is stirred mechanically. Chlorine is run in until the proportion of sodium hypochlorite to sodium hydroxide is greater than one molecule of the former to two of the latter, assuming that all the chlorine reacts according to the equation

$$2Cl + 2NaOH = NaOCl + NaCl + H_2O.$$

[1] This Journal, **41**, 414 (1909).

[2] International atomic weights for 1912 were used in all calculations.

The amount of chlorine added is checked by weighing from time to time.

The free sodium hydroxide in this solution is determined by titration with standard hydrochloric acid. The indicator is not added until the end point is nearly reached in order to avoid as much as possible the action of the hypochlorous acid on it. Tetraiodophenoltetrachlorophthalein was found to give a fairly sharp end point.

The sodium hypochlorite is determined by titration of the iodine liberated from potassium iodide by the hypochlorite in acetic acid solution. One molecule of sodium hypochlorite liberates two atoms of iodine. The iodine is titrated with a standard solution of sodium thiosulphate with an arrowroot starch solution as the indicator.

Sufficient sodium hydroxide is then added to the solution so that it contains two molecules of sodium hydroxide to one of the hypochlorite. This solution may be kept for some little time without undergoing much change.[1]

For the preparation of tetrachloroanthranilic acid according to the method of Villiger and Blangey, 286 grams of the pure, finely pulverized tetrachlorophthalic anhydride is dissolved in 400 cc. of twenty per cent. ammonium hydroxide and the solution poured at once into an excess of dilute sulphuric acid, kept cold by ice. The precipitated tetrachlorophthalamic acid is filtered off as rapidly as possible on a Buchner funnel with suction and washed with water. The moist acid is then dissolved at once in the requisite amount of sodium hydroxide contained in two liters of water and kept cold by ice. It was found that a rapid solution of the tetrachlorophthalamic acid could be effected if it was beaten up in 1500 cc. of water to a milky fluid with a wire beater, 800 grams of ice added, and then a solution of the sodium hydroxide in 500 cc. of water. In this way solution took place almost immediately and a low yield of tetrachloroanthranilic acid due to the hydrolysis of some of the tetrachlorophthalamic acid was prevented. To this mixture the cold sodium hypochlorite solution prepared as described above is added. Sodium hypochlorite

[1] See also Graebe: Ber. d. chem. Ges., **35**, 2753.

is used in ten per cent. excess over the one gram molecule required by the theory for one gram molecule of tetrachlorophthalamic acid. The solution is kept cold by ice added directly and is stirred mechanically. After stirring vigorously for half an hour, the excess of hypochlorite (shown to be present by the blue color produced when a test portion is added to a dilute aqueous solution of aniline) is destroyed by the addition of sufficient sodium bisulphite solution. The solution is then heated for three hours at 70°–80° and decomposed while still hot with an excess of hydrochloric acid. The precipitated acid is quite bulky and is best filtered with suction on a Nutsch filter. The crude acid is then washed with water until free from chlorides. The yield is about ninety per cent.

The pure acid is obtained from the crude product by two methods, one of which was used by Villiger and Blangey. The simpler method is to convert the tetrachloroanthranilic acid into a sodium salt by dissolving it in a boiling ten per cent. solution of sodium carbonate and precipitating the sodium salt by the addition of an equal volume of a saturated solution of sodium chloride. The free acid is obtained by dissolving the sodium salt in hot water and precipitating with a mineral acid. Crystallization of this product from eighty per cent. methyl alcohol gave the pure acid. It has a light yellow color and crystallizes in small needles. About eighty per cent. of the crude material is obtained in this way in the form of the pure acid. The purity of this product was then shown by analyses, after drying to constant weight at 110° in a current of dry air.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1364	19.81	51.50
0.1572	22.87	51.59
	Calculated for $C_7H_3O_2NCl_4$,	51.60

Throughout this investigation chlorine was determined by a modification of the lime method combined with titration according to Volhard.[1] In all cases, unless otherwise stated, the substances prepared for analysis by drying to constant

[1] Delbridge: THIS JOURNAL, 41, 397 (1909).

weight were the air-dried products, and the loss was so small as to be negligible.

The second method for the purification of the crude acid depends upon the formation of the formalide discovered by Villiger and Blangey. This formalide, made and purified as described below, was then converted into the sodium salt of tetrachloroanthranilic acid by boiling with an excess of ten per cent. sodium carbonate solution and adding an equal volume of a saturated salt solution. The sodium salt is filtered off and washed on the filter with a saturated salt solution until free from formaldehyde. The pure acid is then obtained from this sodium salt in the same way as in the first method. The yield by this method is only a little less than in the first, since the precipitation of the formalide is nearly quantitative. The acid is best crystallized by dissolving 100 grams in 300 cc. of boiling methyl alcohol, adding 75 cc. of hot water, and allowing to stand. The material obtained by the second method of purification was analyzed after drying to constant weight at 110°.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1478	21.46	51.49
0.1384	20.13	51.58
	Calculated for $C_7H_3O_2NCl_4$,	51.60

The drying apparatus used during this investigation deserves a brief description because of its simplicity and great convenience, although no claim is made for originating the idea.[1]

A Jena-glass tube, 50 cm. in length and 14 mm. in internal diameter, is wrapped with a layer of heavy asbestos paper for 36 cm. of its length so as to leave both ends uncovered for about 7 cm. Ten or twelve feet of manganin wire about 0.5 mm. in diameter is wound along the tube over the protecting layer of asbestos. A piece of air-cell asbestos steam-pipe covering encloses the wiring, the ends of the covering being sealed with asbestos packing. The apparatus is connected with the alternating current 110-volt lighting circuit,

[1] Chamot and Pratt: J. Am. Chem. Soc., **32**, 635 (1910).

the current passing being varied by means of a lamp rheostat. A current of one ampere will maintain a temperature in the tube of about 100°. Temperatures up to 400° are very easily obtained. The substance for examination is put in a small boat and this boat is introduced into the tube. A slow stream of the desired gas is passed through the tube, and the temperature is observed by means of a thermometer laid in the tube and supported at the posterior opening of the tube by a loosely fitting stopper. This apparatus has all the advantages of that described by Delbridge,[1] and in addition eliminates the danger of fire and the inconvenience of water connections, and offers a much more rapid variation of temperature.

Tetrachloroanthranilic acid may be titrated as a monobasic acid, since the amino group has practically no basic properties, and the purity of the substance may be checked by a determination of the molecular weight. For this purpose the sample, after drying to constant weight at 110°, is dissolved in 10 cc. of neutral alcohol, about 0.5 cc. less than the required amount of tenth normal sodium hydroxide added, the solution diluted with water to about 200 cc., and boiled to expel carbon dioxide. After cooling to about 50°, phenoltetrachlorophthalein is added as the indicator, and the titration completed. Tetrachloroanthranilic acid purified by the first method and analyzed as above for chlorine gave the following results:

Substance Gram	Tenth normal sodium hydroxide cc.	Molecular weight
0.6193	22.48	275.5
0.5465	19.85	275.3
	Calculated for $C_7H_3O_2NCl_4$,	274.9

Dimethylaminoazotetrachlorobenzene-o-carboxylic Acid

Tetrachloroanthranilic acid is an inner ammonium salt, and hence may be diazotized directly. The diazonium salt thus obtained may be combined with dimethylaniline to form the azo compound.

Materials were used in the following proportions:

[1] THIS JOURNAL, 41, 403 (1909).

		Grams
Tetrachloroanthranilic acid	0.05 mol.	13.8
Sodium carbonate	0.025 mol.	2.7
Sodium nitrite	0.05 mol. + 0.1 g.	3.6
Hydrochloric acid	0.20 mol.	7.3
Dimethylaniline	0.05 mol.	6.0

The tetrachloroanthranilic acid was dissolved in 200 cc. of a hot soda solution containing 2.7 grams of sodium carbonate. This solution was cooled to 0°, 3.6 grams of solid sodium nitrite added, and then about 20 cc. of approximately six normal hydrochloric acid containing 3.7 grams of hydrochloric acid. The mixture became pasty, so it was stirred up in about 1.5 liters of water cooled with ice. A solution of dimethylaniline hydrochloride, prepared by dissolving 6.0 grams of dimethylaniline in about 20 cc. of six normal hydrochloric acid, was run into the mixture of the diazonium salt, which was stirred mechanically. Potassium hydroxide solution was added to alkaline reaction, the mixture stirred for six hours and allowed to stand overnight. The azo compound was precipitated by the addition of hydrochloric acid, the mixture being heated almost to boiling for one hour to completely decompose the potassium salt. The precipitate was filtered off with suction and washed free from chlorides. The yield was about ninety per cent.

The crude product was purified by dissolving in hot dilute potassium hydroxide, from which solution the potassium salt crystallizes on cooling. This salt was filtered off, dissolved in hot water, and decomposed with hydrochloric acid. The decomposition was rendered complete by boiling for one hour. The precipitated azo compound was filtered off with suction and washed free from chlorides.

After drying to constant weight at 120° the substance was analyzed for chlorine:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1966	19.19	34.61
0.2130	20.82	34.66
Calculated for $C_6Cl_4\begin{matrix}N : N.C_6H_4.N(CH_3)_2,\\ COOH\end{matrix}$		34.85

Dimethylaminoazotetrachlorobenzene-*o*-carboxylic acid is a brilliant red substance, almost insoluble in all ordinary solvents. It is the tetrachloro derivative of methyl red, which was found to possess valuable properties as an indicator.[1] An attempt to use this product as an indicator with tenth normal solutions of ammonium hydroxide, sodium hydroxide and hydrochloric acid showed that the substance was of no value in this respect since the end point was indefinite and not rapidly obtained, the color change was not marked and the reagent lacked sensitiveness to small excesses of the acid or alkali.

Tetrachloroanthranilic Acid Formalide

Villiger and Blangey[2] obtained tetrachloroanthranilic acid formalide by the condensation of tetrachloroanthranilic acid with formaldehyde, and have briefly described the method of preparation and properties of the substance.

During this investigation it was necessary to prepare large quantities of the formalide, the following procedure being found to give the best results: 100 grams of the acid is dissolved in 500 cc. of hot alcohol, 33 grams of thirty-six per cent. formalin added, and the mixture allowed to stand at about 10° for several hours. The formalide crystallizes out in light yellow shimmering leaflets, melting at 213°. Repeated crystallization from alcohol and benzene did not change the color or melting point of the substance, although Villiger and Blangey describe it as being white and melting at 216°. The product which crystallizes out of the reaction mixture is perfectly pure, and a yield of about ninety-five per cent. is obtained. A small quantity of a less pure product may be recovered by concentrating the mother liquor. The corrected melting point of the formalide was found to be 216°. The substance was analyzed for chlorine after drying to constant weight at 110° in hydrogen:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1394	19.42	49.40
	Calculated for $C_8H_3O_2NCl_4$,	49.44

[1] Rupp and Loose: Ber. d. chem. Ges., **41**, 3905 (1908).
[2] *Ibid.*, **42**, 3551 (1909).

Melting point determinations throughout this investigation were made with an electrically heated Thiele apparatus. Platinum wire was wrapped about the side-arm of the Thiele tube, which was covered with a layer of asbestos to prevent too severe local heating. The wiring was enclosed in a jacket of asbestos fiber cement. The apparatus was connected to the alternating current lighting circuit, the current passing being controlled by a lamp rheostat. The rate of change of temperatures may be easily regulated, and the conditions in different runs maintained uniform without any difficulty. No claim for originality is made in devising this apparatus, which was introduced in this laboratory by Dr. D. S. Pratt.

Tetrachloroanthranilic Acid Formalide Acetate

The imino hydrogen atom of tetrachloroanthranilic acid formalide may be replaced by the acetyl group by heating with acetic anhydride. The acetylation was brought about by boiling 10 grams of the formalide with 150 grams of acetic anhydride for about three hours. On pouring the resultant solution into ice water an oil separated which quickly solidified. The crude product was obtained as a light yellowish brown substance. The yield was ninety per cent.

The crude material was crystallized from alcohol and then from benzene. The melting point of the product from alcohol was not changed by recrystallization from benzene. The acetate crystallizes in colorless rectangular plates melting at 166°.5 (cor.).

The substance crystallized from benzene was dried to constant weight at 110° and analyzed for chlorine:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1691	20.52	43.03
Calculated for $C_8H_2O_2NCl_4(C_2H_3O)$,		43.13

ω-Cyanomethyltetrachloroanthranilic Acid

This cyano compound is referred to very briefly by Villiger and Blangey, who state[1] simply that a solution of potassium cyanide gradually dissolves the formalide with the forma-

[1] Ber. d. chem. Ges., **42**, 3552 (1909).

tion of the potassium salt of ω-cyanomethyltetrachloroanthranilic acid, $C_6Cl_4\langle^{NH.CH_2.CN}_{COOH}$.

They describe the acid as crystallizing in needles melting at 178°, and they state that on boiling with sodium hydroxide it is converted into the corresponding dicarboxylic acid.

The reaction between the formalide and potassiun cyanide must be brought about at comparatively low temperatures since on warming the solution the formalide is decomposed into its components. The best results were obtained by suspending 100 grams of the formalide in one liter of a ten per cent. solution of potassium cyanide. The mixture was stirred mechanically at room temperature for one-half hour, at the end of which time solution was practically complete. The potassium salt of the cyanomethyl compound may crystallize out, but can be easily redissolved by adding more water. The filtered solution was acidified with hydrochloric acid and allowed to stand for several hours. The cyano compound was precipitated in part in crystalline form and in part as an oil which soon solidified. The product was filtered off with suction and washed free from chlorides. The yield was about ninety-five per cent. The reaction is apparently quantitative, but the solubility of the compound in water lowers the yield.

The pure substance was obtained by one crystallization of the crude product from water. Two hundred parts of hot water dissolves one part of the cyano compound, and on cooling most of the material crystallizes out. This product melts at 176° (uncor.). It is almost white with a slight tinge of yellow. It is very readily soluble in cold alcohol, benzene and acetone, less readily soluble in ether and chloroform, insoluble in petroleum ether. The air-dried product was heated to constant weight at 110° in a current of dry air, the loss in weight being inconsiderable, and was then analyzed for chlorine.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1669	21.26	45.17
0.1797	22.89	45.17
	Calculated for $C_9H_4O_2N_2Cl_4$,	45.19

Tetrachlorophenylglycine-o-carboxylic Acid

Reference has been made above to the fact that Villiger and Blangey state that ω-cyanomethyltetrachloroanthranilic acid yields the corresponding dicarboxylic acid on hydrolysis. The Badische Anilin- und Soda-Fabrik have patented[1] this method of making tetrachlorophenylglycine-*o*-carboxylic acid. In the patent the substance is described as crystallizing from hot water in white needles melting at 198° with decomposition.

Mauthner and Suida[2] prepared phenylglycine-*o*-carboxylic acid by the reaction between anthranilic acid and monochloroacetic acid in the presence of an excess of sodium carbonate. Later Heumann[3] made it by boiling an aqueous solution of anthranilic acid with monochloroacetic acid without the use of sodium carbonate.

An attempt to prepare tetrachlorophenylglycine-*o*-carboxylic acid by Mauthner and Suida's method showed that the reaction proceeded to some extent at least, but the yield was small and the difficulty of purifying the product rendered the method of no value. The comparative insolubility of tetrachloroanthranilic acid in water prohibited the use of Heumann's method.

The preparation of pure tetrachlorophenylglycine-*o*-carboxylic acid necessitates the complete hydrolysis of pure ω-cyanomethyltetrachloroanthranilic acid. This is best brought about by dissolving the cyano compound in a five per cent. sodium hydroxide solution containing about three molecular parts of sodium hydroxide to one of the cyano compound. The alkaline solution is then heated to boiling and distilled in steam until ammonia no longer distils over. Five hours or more may be required to drive out all the ammonia. An equal volume of water is added, and the mixture filtered to get rid of a small quantity of a greenish blue substance, and also silica from the glass apparatus. The filtrate is acidified with hydrochloric acid and allowed to stand several

[1] Chem. Zentralb., **1910**, I, 1564. D. R. P. Kl. 12 q. Nr. 220839.
[2] Monats. Chem., **9**, 728 (1888).
[3] Ber. d. chem. Ges., **23**, 3432 (1890).

hours. The precipitate is filtered off and washed free from chlorides. The yield is practically quantitative.

The crude product is purified by crystallization from hot water. Boiling water dissolves the acid fairly readily, and on cooling the material is precipitated in the form of very small crystalline needles. The air-dried product is almost white, with a yellow tinge, and melts at 198° (cor.).

The substance crystallized from water and air-dried contains a molecule of water of crystallization, which is given off very readily at 110°. For analysis the material was dried to constant weight at 110° in the drying tube.

Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.4204	0.0216	5.14
0.4480	0.0229	5.11
Calculated for $C_9H_5O_4NCl_4.H_2O$,		5.14

Chlorine in the product dried to constant weight at 110° was determined with the following results:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1360	16.42	42.81
0.1939	23.42	42.83
Calculated for $C_9H_5O_4NCl_4$,		42.61

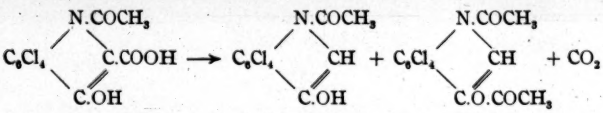
The analyses apparently show that the material is contaminated with a small quantity of the cyano compound, and this conclusion is supported by a determination of the molecular weight. The air-dried substance was used for this purpose:

Substance Gram	Tenth normal sodium hydroxide cc.	Molecular weight
0.2990	16.83	355.3
0.3610	20.26	356.4
Calculated for $C_9H_5O_4NCl_4.H_2O$,		350.9

Acetyl Derivative of Tetrachloroindoxyl

The action of acetic anhydride alone on tetrachlorophenylglycine-*o*-carboxylic acid is to eliminate water with the formation of an acetyl derivative of tetrachloroindoxylic acid as described below. If fused sodium acetate be used with the acetic anhydride, the reaction proceeds further, carbon dioxide

is removed from the carboxyl group, and mono- and diacetates of tetrachloroindoxyl are formed. This may be represented graphically as follows:



The acetyl group in the monoacetate of tetrachloroindoxyl is represented as being attached to the nitrogen since that is its apparent position in tetrachloroindoxylic acid monoacetate.

For the preparation of these acetates tetrachlorophenylglycine-*o*-carboxylic acid is boiled about two hours with an equal weight of fused sodium acetate and five times its weight of acetic anhydride. The resultant solution is poured into ice water and the mixture stirred mechanically. A brown oil is thrown out which quickly solidifies. This product is then filtered off, washed thoroughly with water, and air-dried. The yield is about seventy-five per cent., calculated on the basis of the diacetate.

The two acetates were obtained from the crude material by fractional crystallization from anhydrous ether. The diacetate is not very soluble in ether and separates out of the hot solution on cooling in well crystallized rectangular plates and prisms, the first crystallization yielding a brown product. In this way about fifteen per cent. of the crude product is obtained as the diacetate. By recrystallizing from ether after boiling the solution with boneblack, the substance was obtained with only a very light blue color and melting at 167° (uncor.). This material, after drying to constant weight at 100°, was analyzed for chlorine:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1970	22.06	39.71

Calculated for $C_6HONCl_4(C_2H_3O)_2$, 39.97

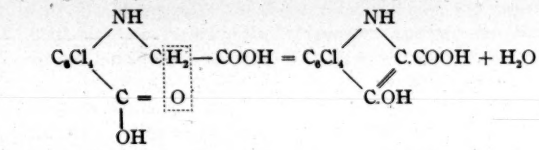
The monoacetate is much more soluble in ether than the diacetate, and is obtained by concentrating the solution after

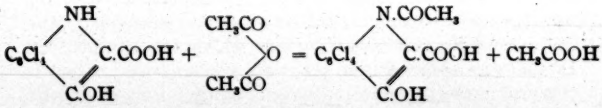
the diacetate has been crystallized out. From ether solutions which have been boiled with boneblack it crystallizes in small rounded masses of slender microscopic prisms, perfectly white, and melting at 195° (uncor.). The substance was dried to constant weight at 110° and analyzed for chlorine:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1356	17.14	44.82
Calculated for $C_8H_3ONCl_4(C_2H_3O)$,		45.33

Tetrachloroindoxylic Acid Monoacetate

It seemed probable that acetic anhydride would withdraw a molecule of water from tetrachlorophenylglycine-*o*-carboxylic acid with the formation of tetrachloroindoxylic acid. This reaction apparently takes place, but an acetylated derivative is produced by the continued action of acetic anhydride. This may be represented graphically as follows:





Vorländer and Drescher state[1] that in the case of indoxylic acid monoacetate the acetyl group is attached to the nitrogen atom since the acetylation may be brought about in acid or alkaline solution with the formation of the same substance. Inasmuch as the acetate may be made in alkaline solution it is reasonable to suppose that the acetyl group must be attached to nitrogen. The analogous tetrachloroindoxylic acid monoacetate is therefore represented with a similar structure. Tetrachloroindoxylic acid monoacetate is prepared by boiling

[1] Ber. d. chem. Ges., 34, 1854 (1901).

tetrachlorophenylglycine-*o*-carboxylic acid with about five times its weight of acetic anhydride for at least one hour, and pouring the resultant solution into ice water. A green oil is thrown out which solidifies in a short time. The mixture is kept stirred mechanically so as to assist in washing out acetic anhydride. The precipitate is filtered off, washed by stirring with water for an hour, and again filtered off. The crude product thus obtained is light green. The yield is variable, but under favorable conditions is about eighty-five per cent. The filtrates, which are strongly acid with acetic acid, hold some of the material in solution, and this may be recovered by evaporating to dryness. The yield is then almost quantitative, but a blue coloring matter is always formed as a by-product.

The crude product is extracted first with a small quantity of benzene to remove most of the coloring matter. Some of the acetate is dissolved by the benzene, but this may be recovered in part by crystallization from the solution. The residue after extraction is crystallized from anhydrous ether. Solvents containing the hydroxyl group, or those not perfectly anhydrous, apparently decompose the acetate to some extent, and highly colored products result. Repeated crystallization from ether yields the pure substance in the form of a crystalline powder, faintly yellowish green, melting at 225° (cor.) with the evolution of gas. The melting point must be determined rapidly because of the decomposition which takes place with consequent lowering of the melting point.

The pure acetate thus obtained was dried to constant weight at 110° and analyzed for chlorine and nitrogen:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1754	19.61	39.65
0.1838	20.62	39.78
Calculated for $C_9H_2O_3NCl_4(C_2H_3O)$,		39.74

Nitrogen was determined by the Kjeldahl method with the following result:

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.4854	13.45	3.88
Calculated for $C_9H_2O_3NCl_4(C_2H_3O)$,		3.93

The presence of the carboxyl group is indicated by the ease with which the acetate dissolves in cold caustic alkali. The substance does not undergo any change, for on acidification of the alkaline solution the original material is precipitated. Warming with sodium carbonate solution dissolves and saponifies the material, and then with continued heating and shaking in the air a quantitative precipitation of octochloroindigo results.

Silver Salt of Tetrachloroindoxylic Acid Monoacetate

The formation of a stable silver salt of tetrachloroindoxylic acid monoacetate confirms the conclusion that the acetate contains a carboxyl group. The correct conditions for the preparation of this salt were found to be of very great importance if a pure product was to be obtained, since the impure material cannot be purified. The following procedure gave satisfactory results.

One gram of the pure acetate was dissolved in sixty cc. of hot alcohol (distilled over silver nitrate), the solution filtered and allowed to stand for ten hours. At the end of this time the small amount of material that had separated out was filtered off, and to the filtrate was added sixty-five cc. of an alcoholic solution of silver nitrate containing about thirty grams of silver nitrate per liter. This is about four times the amount of silver nitrate required by the theory. A large excess of silver nitrate is, however, essential in order to obtain the pure silver salt. After several days the silver salt, which had slowly crystallized out in ball-like clusters of small needles, was filtered off, washed with cold alcohol, and allowed to air-dry. The product was light grayish green, and analysis for silver showed it to be pure. The air-dried substance contains a molecule of water of crystallization. This was determined by heating the material to constant weight at 110° in carbon dioxide. The condensation of moisture on the walls of the cool part of the tube was observed.

Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.3755	0.0130	3.46

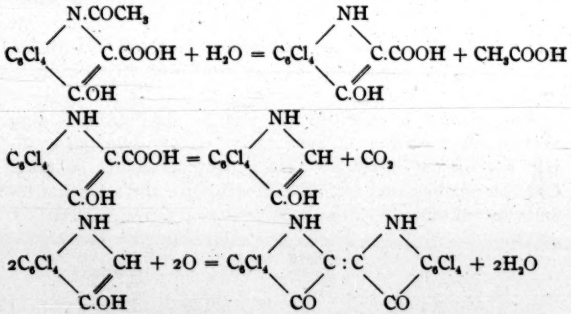
Calculated for $C_9HO_2NCl_4(C_2H_3O)Ag.H_2O$, 3.74

The portion used for determining the loss of weight was then analyzed for silver. This was carried out by suspending the substance in 100 cc. of boiling alcohol and decomposing with about 10 cc. of dilute nitric acid. The liberated organic acid and the silver nitrate formed are both soluble in alcohol, so that a clear solution was obtained which was light green. The silver nitrate present was titrated directly with tenth normal ammonium sulphocyanate, using ammonium ferric sulphate as indicator. The color of the original solution does not interfere with the sharpness of the end point.

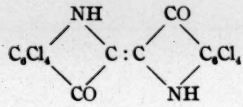
Substance Gram	Tenth normal ammonium sulphocyanate cc.	Silver Per cent.
0.3624	7.74	23.04
Calculated for $C_9HO_3NCl_4(C_2H_3O)Ag$,		23.26

Octochloroindigo

A quantitative precipitation of octochloroindigo occurs when alkaline solutions of tetrachloroindoxylic acid monoacetate are boiled and aërated. The reaction consists in the hydrolysis of the acetate, the elimination of carbon dioxide from the carboxyl group and the oxidation of the resulting tetrachloroindoxyl. This may be represented by the following scheme:



Attention is called to the possibility of stereoisomeric modifications of indigo. The *cis* form of octochloroindigo is shown above; the *trans* form would be represented as follows:



The possible stereoisomerism of indigo has been previously suggested by Falk and Nelson.[1]

Because of the difficulty of purifying octochloroindigo, it is desirable in its preparation to start with pure materials and to use a method which introduces the least possible amount of foreign material. Ammonium hydroxide proved itself to be the most satisfactory alkaline substance to bring about the reaction. Five grams of the pure acetate was dissolved in 250 cc. of four normal ammonium hydroxide with the aid of heat. On continued heating of the solution a green flocculent precipitate was thrown down. The mixture was diluted with water to about two liters and boiled for one hour, while a fairly rapid current of air was passed through it. At the end of this time the green precipitate had entirely changed in color to blue. In order to be sure that the reaction had been complete, twenty-five cc. more of ammonium hydroxide was added and the boiling continued one hour longer. The blue material was quite bulky, and had formed an apparently permanent suspension which did not settle on standing. It was filtered off with suction and washed on the filter with hot water until the wash water left no residue on evaporating to dryness.

The reaction is quantitative, and so starting with pure acetate and removing the ammonium salts by thorough washing, the product obtained by this method should be pure. Octochloroindigo prepared in this way gave the following results for chlorine and nitrogen after drying to constant weight at 110°:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1353	20.07	52.60
0.1443	21.28	52.29
Calculated for $C_{16}H_2O_2N_2Cl_8$,		52.76

[1] J. Am. Chem. Soc., **29**, 1739 (1907). See also Ber. d. chem. Ges., **28**, 539 (1895).

Nitrogen was determined by the Kjeldahl method.

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.2888	10.82	5.25
0.3374	13.26	5.51
	Calculated for $C_{16}H_2O_2N_2Cl_8$,	5.21

Octochloroindigo as prepared by the above method is amorphous, with a rich purple color, and having also a coppery luster which is especially noticeable when the substance is rubbed. Heated at 360° in a current of air it sublimes with some decomposition. The sublimate is finely crystallized in rhombic plates, which are green in thin layers, changing to red and then blue with increasing thickness. The amorphous material dissolves in cold concentrated sulphuric acid with a green color, and the color deepens when the solution is warmed, no other change being apparent. The purple octochloroindigo is precipitated evidently unchanged when this solution is poured into water. The substance dissolves in aniline with a green color. The hot nitrobenzene solution is blue, but on cooling the color changes to green and most of the material crystallizes out, although the crystals are not well developed. It dissolves readily in dimethylaniline with a blue color, and crystallizes from the hot solution on cooling. The product thus obtained is homogeneous, and the fusiform crystals are microscopic in size and very well formed.

Hydroxylamine Derivatives of Tetrachlorophthalic Anhydride

According to Villiger and Blangey dichlorophthalylhydroxylamine (or better, dichlorophthaloxime) may be very easily converted into dichloroanthranilic acid by boiling with a solution of sodium carbonate.[1] This suggested a convenient method for the preparation of tetrachloroanthranilic acid from the corresponding tetrachlorophthaloxime. The peculiar problems presented by the reactions between tetrachlorophthalic anhydride and hydroxylamine seemed to warrant a more detailed study of the subject.

[1] Ber. d. chem. Ges., **42**, 3543 (1909).

Methyl Ether of Tetrachlorophthaloxime Hydrate

It was supposed that hydroxylamine would react most advantageously if all of the reacting substances were in solution. Materials were used in the following proportions:

		Grams
Hydroxylamine hydrochloride	0.2 mol. + 25 per cent. excess	17.4
Sodium	0.2 mol. + 25 per cent. excess	5.8
Tetrachlorophthalic anhydride	0.2 mol.	57.2

A methyl alcohol solution of hydroxylamine was made by dissolving the hydroxylamine hydrochloride in about 100 cc. of methyl alcohol and pouring this solution into a solution of sodium methylate prepared by dissolving the metallic sodium in 400 cc. of methyl alcohol. The precipitated sodium chloride was filtered off. To the filtrate was added a solution of the anhydride in 250 cc. of methyl alcohol.

The mixture was boiled for one hour under a return condenser, and then concentrated to about 200 cc. The sodium chloride which was precipitated was filtered off, and the filtrate was diluted strongly with water. This was then evaporated to dryness on the water bath. The residue was extracted with boiling benzene to remove unchanged anhydride. The bulk of the residue was insoluble in benzene. It was fairly readily soluble in methyl alcohol, and crystallized very well from this solvent in small rhombic plates. The crystalline material has a decided yellow color. It melts at 246°–247° (cor.) with decomposition. After drying to constant weight at 110° it was analyzed for chlorine and nitrogen.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1555	18.70	42.64
Calculated for $C_8H_2O_3Cl_4N(OCH_3)$,		42.61

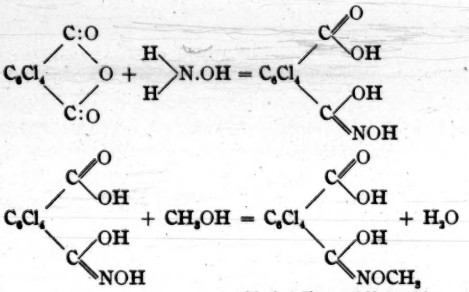
Nitrogen in the hydroxylamine compounds was determined by a modified Kjeldahl method. The portion for analysis was first reduced with nascent hydrogen by boiling for half an hour in the Kjeldahl digestion flask with 3 grams of zinc dust and 50 cc. of thrice normal sulphuric acid. Concentrated sulphuric acid, potassium sulphate and copper sul-

phate were then added as in the usual method, and the digestion carried on for an hour or so until the reaction was completed.

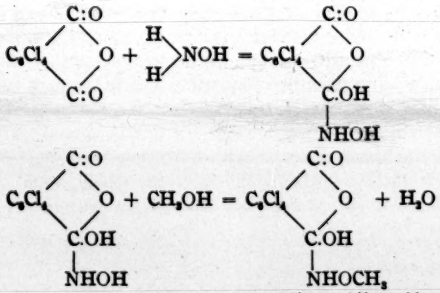
Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.4743	14.23	4.20

Calculated for $C_9H_2O_3NCl_4(OCH_3)$, 4.21

The methyl ether of tetrachlorophthaloxime hydrate is isomeric with the methyl ester of tetrachlorophthalhydroxamic acid. The formation of either of these substances in the above reaction may be shown by the use of structural formulas as follows:



Methyl Ester of Tetrachlorophthalhydroxamic Acid



Methyl Ether of Tetrachlorophthaloxime Hydrate

It seems probable that the latter reaction is the one which actually takes place, since the product does not dissolve in cold caustic alkali, but is converted into an insoluble red substance in aqueous alkaline solutions. Of special importance is the fact that no coloration is produced with ferric chloride. Since hydroxamic acids should always give a violet color with this reagent, it is not likely that this substance is the methyl ester of tetrachlorophthalhydroxamic acid. The material does not lose water when heated to 160°, but at that temperature it sublimes somewhat.

An attempt to prepare a sodium salt resulted in the formation of an impure salt of tetrachlorophthaloxime. Two grams of the ether was dissolved in 200 cc. of methyl alcohol and to the hot solution was added a solution of one gram of fused sodium acetate in 50 cc. of methyl alcohol. The mixture became red, and on concentrating to about 100 cc. and cooling, a red crystalline product was obtained. This was dried in the water oven and then to constant weight at 120° in the drying apparatus. Analysis for chlorine gave the following result:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1644	20.83	44.93
Calculated for $C_8O_3Cl_4NNa$,		43.93
Calculated for $C_8HO_3Cl_4N(OCH_3)Na$,		39.97

It is hardly reasonable to suppose that boiling the sodium salt of the methyl ester of tetrachlorophthalhydroxamic acid with a small quantity of sodium acetate in methyl alcohol solution would result in the elimination of a molecule of methyl alcohol. On the other hand, it seems probable that under similar conditions the methyl ether of tetrachlorophthaloxime hydrate might be hydrolyzed, with the formation of the sodium salt of tetrachlorophthaloxime hydrate, which could then very easily lose water and yield the anhydrous product.

Tetrachlorophthaloxime Hydrate and Tetrachlorophthaloxime

Quite a different product was obtained when water was used as the medium from that which resulted when the reaction

between hydroxylamine and tetrachlorophthalic anhydride was carried out in methyl alcohol solution. Recently, in this laboratory, Dr. D. S. Pratt[1] found that in the case of phthalic anhydride the temperature employed exerted a great influence on the nature of the substances formed. If the reaction mixture was heated in the water bath, the phthaloxime obtained was yellow, but if the reaction proceeded at 60° a white isomer was formed. Attempts were made to duplicate these results with tetrachlorophthalic anhydride.

Materials were used in the following proportions:

		Grams
Hydroxylamine hydrochloride	0.2 mol. + 25 per cent. excess	17.4
Sodium carbonate, anhydrous	0.1 mol. + 25 per cent. excess	13.3
Tetrachlorophthalic anhydride	0.2 mol.	57.2

The hydroxylamine hydrochloride was dissolved in 50 cc. of cold water, the sodium carbonate in 50 cc. of hot water. After cooling, the soda solution was poured into the hydroxylamine hydrochloride solution, which was contained in a one liter round-bottomed flask. The anhydride was then rapidly added to this mixture, care being taken at the start, however, not to cause too violent an evolution of gas. The flask was then immersed in an actively boiling water bath and heated in this way without stirring for one hour. The thick, pasty reaction mixture was taken up with water, made decidedly acid with hydrochloric acid and filtered with suction. The residue on the filter was washed with water and then dissolved without drying in methyl alcohol acidified with hydrochloric acid. Acidification is resorted to in order to decompose any sodium salt of the oxime that might have been formed. The reaction product is not very soluble in cold methyl alcohol, and since tetrachlorophthalic anhydride is exceedingly soluble the unchanged anhydride is easily separated from the other material. The yield from the first crystallization was thirty grams, about fifty per cent. of the theoretical. The pure sub-

[1] THIS JOURNAL, 47, 89 (1912).

stance was obtained by recrystallizing this product from methyl alcohol.

This material is almost perfectly white, but has a faintly yellow tinge. It crystallizes in small prisms and melts at 254° (cor.). The air-dried material was heated to constant weight at 110°. The formation of water was shown by the condensation of moisture on the cold part of the tube.

Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.1678	0.0094	5.60
0.4774	0.0271	5.68
	Calculated for $C_8HO_3NCl_4.H_2O$,	5.65

The ease with which this substance loses water was shown by heating it at 50° in a current of hydrogen dried by phosphorus pentoxide. The material came to constant weight in three hours.

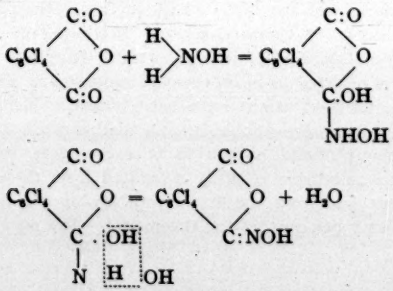
Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.1703	0.0096	5.64

Standing for twenty-one hours in an evacuated desiccator with phosphorus pentoxide above and below also removed the water, the sample coming to constant weight.

Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.2649	0.0151	5.70

The anhydrous product was lemon-yellow.

The substance is apparently a stable hydroxylamine addition product of tetrachlorophthalic anhydride. The reaction is represented as follows:



We have called this addition product tetrachlorophthaloxime hydrate. As has been seen, it readily loses a molecule of water and yields the anhydrous tetrachlorophthaloxime. It is analogous to the chloral-hydroxylamine of Hantzsch,[1] which is the hydroxylamine addition product of chloral. The presence of the chlorine in the molecule gives rise to the possibility of the existence of the stable hydrates. Chlorine and nitrogen in the anhydrous substance were determined with the following results:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1576	21.02	47.29
0.1553	20.69	47.24
	Calculated for $C_8HO_3NCl_4$,	47.15

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.3454	11.84	4.80
0.4494	14.91	4.65
	Calculated for $C_8HO_3NCl_4$,	4.66

Tetrachlorophthaloxime made by heating the crystallized hydrate has the same outward crystal form as the hydrate, but has a pronounced yellow color. It crystallizes from anhydrous benzene with a yellow color. Alkalis convert it as well as the hydrate into the red salts of the oxime, which are insoluble in water. These salts are easily decomposed by warming with caustic alkalis, tetrachlorophthalic acid being formed. Standing with caustic alkalis in the cold, or prolonged boiling with sodium carbonate solution converts the alkali salts into the salts of tetrachlorophthalhydroxamic acid which are colorless and readily soluble in water. No formation of tetrachloroanthranilic acid could be observed. The melting point given for the hydrate is really that of the anhydrous substance since the latter is formed during the heating.

Sodium Salt of Tetrachlorophthaloxime

The yellow oxime was very easily converted into the pure sodium salt. This was accomplished by boiling 5 grams of

[1] Ber. d. chem. Ges., **25**, 702 (1892).

the oxime in 500 cc. of methyl alcohol with sodium acetate in considerable excess. The sodium salt was precipitated in crystalline form. The mixture was boiled for an hour to insure the complete formation of the salt. The material separated out in rounded clusters of threadlike crystals, dark red in color. This product was filtered off with suction and washed with methyl alcohol.

The substance was analyzed for chlorine and sodium after drying to constant weight at 150°.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1528	18.82	43.68
	Calculated for $C_8O_3NCl_4Na$,	43.93

Sodium was determined by fuming down with sulphuric acid. The portion for analysis was contained in a platinum crucible, and to it was added two or three cc. of concentrated sulphuric acid. The crucible was heated in an air bath made of a larger nickel crucible, 85 mm. deep, 105 mm. wide at the top. The platinum crucible was supported on a quartz triangle at a height of about 40 mm. from the bottom of the nickel crucible. The nickel crucible was heated with a moderate sized Bunsen flame, and kept nearly closed by the crucible cover. One cc. of concentrated sulphuric acid was added from time to time as the concentration proceeded until the solution became colorless. An excess of sulphuric acid should always be present to prevent reduction of the sodium sulphate by unburned carbon and consequent loss of sodium by volatilization. The colorless solution was evaporated to dryness in the apparatus, and then the platinum crucible was heated directly for a short time with a Bunsen flame.

Substance Gram	Sodium sulphate Gram	Sodium Per cent.
0.3009	0.0658	7.08
0.2830	0.0640	7.32
	Calculated for $C_8O_3NCl_4Na$,	7.12

Tetrachlorophthaloxime Acetate

The oxime hydrate was boiled for an hour with four or five times its weight of acetic anhydride. The solution was poured

into ice water with mechanical stirring, and the product washed with water until practically free from acetic acid. The crude material, which was fairly white, was filtered off and air-dried. When thoroughly dry it was crystallized from anhydrous ether. The pure acetate was obtained by the first crystallization. It crystallizes in white needles, melting at 176° (cor.). The acetate is very easily saponified, even standing with ninety-five per cent. alcohol bringing about the saponification. It may be obtained well crystallized from absolute alcohol, in which it is quite soluble hot, but much less soluble cold. It is excessively soluble in benzene.

The substance from ether was analyzed for chlorine and nitrogen after drying to constant weight in a current of hydrogen.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1762	20.55	41.36
Calculated for $C_9O_3Cl_4N(C_2H_3O)$,		41.37

The acetate was saponified by gentle warming with potassium hydroxide, and the nitrogen determined in this product in the usual way.

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.4031	11.81	4.11
Calculated for $C_9O_3Cl_4N(C_2H_3O)$,		4.09

SUMMARY

The results of this investigation may be briefly stated as follows:

The following substances, which have previously been more or less completely described, have been prepared:

Tetrachloroanthranilic acid

Tetrachloroanthranilic acid formalide

ω-Cyanomethyltetrachloroanthranilic acid

Tetrachlorophenylglycine-*o*-carboxylic acid

The following new substances have been made and studied:

Tetrachloroanthranilic acid formalide acetate

Dimethylaminoazotetrachlorobenzene-*o*-carboxylic acid

Tetrachloroindoxyl monoacetate

Tetrachloroindoxyl diacetate
Tetrachloroindoxylic acid monoacetate
Tetrachloroindoxylic acid monoacetate, silver salt
Octochloroindigo
Methyl ether of tetrachlorophthaloxime hydrate
Tetrachlorophthaloxime hydrate
Tetrachlorophthaloxime (yellow)
Tetrachlorophthaloxime, sodium salt
Tetrachlorophthaloxime acetate

CORNELL UNIVERSITY
ITHACA, N. Y.
October, 1912

THE CONDUCTIVITY, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND DISSOCIATION OF CERTAIN ELECTROLYTES IN AQUEOUS SOLUTION AT 35°, 50° AND 65°

BY S. F. HOWARD AND HARRY C. JONES

INTRODUCTION

Hosford and Jones[1] and Miss Winston and Jones[2] have measured the conductivity, temperature coefficients of conductivity and dissociation of many electrolytes between 0° and 35°. To extend some of these measurements to higher temperatures, to ascertain whether certain observations made by them at lower temperatures obtain for higher temperatures, and to account, if possible, for certain discrepancies have been the aims of this investigation.

HISTORICAL

Conductivity measurements were made soon after Galvani's discovery of "animal electricity" (1789), and Volta's recognition (1793) of the two classes of conductors, one class conducting apparently without being changed chemically, while conductors of the second class were decomposed by the passage of the current.

Although the study of conductors of the second class did not, for many years, lead to a satisfactory explanation of the

[1] THIS JOURNAL, **46**, 240 (1911).
[2] *Ibid.*, **46**, 368 (1911).

phenomena of conduction in solution, certain important relations were discovered.

Davy began investigations[1] in 1800 which led to the isolation of the alkali and alkaline earth metals and to the decomposition of water into hydrogen and oxygen. This work and that of others along the same lines led to the electrochemical theories of Davy[2] and Berzelius,[3] and later to the announcement of Faraday's law.[4]

Faraday recognized that solutions of certain substances conducted the current, whereas those of others did not. The former he termed electrolytes and the latter nonelectrolytes. He saw, moreover, that the electrolytes decomposed into charged parts. Those parts which were charged negatively he termed anions, and those that were positively charged were called cations.

A large number of salts, acids and bases were studied by many workers, but the significance of conductivity was not understood until the theory of Arrhenius[5] was proposed in 1887. This theory not only gave added interest and significance to the conductivity of solutions, but brought together under one generalization many of the abnormal measurements of osmotic pressure and of vapor tension and of freezing point lowering. The incentive to make conductivity measurements was greatly increased by the theory, especially as it was pointed out that dissociation could be measured when the conductivity was known at a given dilution and at infinite dilution.

That is, $\alpha = \mu_v/\mu_\infty$, where α is the dissociation, μ_v the conductivity at volume v, and μ_∞ the conductivity at complete dissociation or infinite dilution.

Since the measurements of conductivity can be interpreted in terms of the strengths of acids and bases, and since the reactions between various salts and acids, bases and other salts are conditioned by the amount of ionization, it is evident that a knowledge of these constants is desirable.

[1] Phil. Trans., **1807**, 2.
[2] *Ibid.*, p. 39.
[3] Gilb. Ann., **27**, 270 (1807).
[4] Exp. Researches in Elec., 1833–4.
[5] Z. physik. Chem., **1**, 631 (1887).

The theory of solvation proposed by Jones[1] and confirmed by many lines of experiments conducted by him and his coworkers added further interest to conductivity measurements by explaining very satisfactorily, and for the first time, many apparent abnormalities.

Previous to the work of Kohlrausch,[2] conductivity measurements were made by means of direct currents, but because of polarization the results were not accurate. A considerable number of conductivity measurements have been made since the Kohlrausch method was proposed, but little systematic work was done until Jones and his coworkers took up the problem.

The work in this laboratory has been carried on systematically, measurements being made upon solutions of most of the more common electrolytes, at temperatures from 0° to 65°, and at convenient and uniform dilutions. When the work as a whole is completed there will be obtainable many data which have heretofore not been available.

[1] 1. Jones and Chambers: THIS JOURNAL, **23**, 89 (1900). 2. Chambers and Frazer: *Ibid.*, **23**, 512 (1900). 3. Jones and Getman: *Ibid.*, **27**, 433 (1902). 4. Jones and Getman; Z. physik. Chem., **46**, 244 (1903); Phys. Rev., **18**, 146 (1904). 5. Jones and Getman: THIS JOURNAL, **31**, 303 (1904). 6. Jones and Getman: Z. physik. Chem., **49**, 385 (1904). 7. Jones and Getman: Ber. d. chem. Ges., **37**, 1511 (1904). 8. Jones and Getman: THIS JOURNAL, **32**, 308 (1904). 9. Jones and Getman: *Ibid.*, **32**, 338 (1904). 10. Jones and Bassett: *Ibid.*, **33**, 534 (1905). 11. Jones: J. chim. phys., **3**, 455 (1905). 12. Jones and Bassett: Z. physik. Chem., **52**, 231 (1905). 13. Jones and Bassett: THIS JOURNAL, **34**, 291 (1905). 14. Jones: Z. physik. Chem., **35**, 385 (1906). 15. Jones and McMaster: THIS JOURNAL, **35**, 136 (1906). 16. Jones: *Ibid.*, **35**, 445 (1906). 17. Jones and Uhler: *Ibid.*, **37**, 126 (1907). 18. Jones and Uhler: *Ibid.*, **37**, 244 (1907). 19. Jones and Pearce: *Ibid.*, **38**, 683 (1907). 20. Jones and Stine: *Ibid.* **39**, 313 (1908). 21. Jones and Anderson: P. Am. Phil. Soc., **47**, 276 (1908). 22. Jones and Jacobson: THIS JOURNAL, **40**, 355 (1908). 23. Jones: *Ibid.*, **41**, 19 (1909). 24. Jones and Anderson: *Ibid.*, **41**, 163 (1909). 25. Jones and Anderson: P. Am. Phil. Soc., **48**, 194 (1909). 26. Jones and Strong: THIS JOURNAL, **43**, 37 (1910). 27. Jones and Strong: Physik. Z., **10**, 499 (1909). 28. Jones and Strong: THIS JOURNAL, **43**, 224 (1910). 29. Jones and Strong: Phil. Mag., **1910**, 566. 30. Jones: Z. physik. Chem., **74**, 325 (1911). 31. Jones and Schmidt: THIS JOURNAL, **43**, 37 (1909). 32. White and Jones: *Ibid.*, **43**, 520 (1909). 33. Clover and Jones: *Ibid.*, **43**, 187 (1910). 34. White and Jones: *Ibid.*, **44**, 159 (1910). 35. West and Jones: *Ibid.*, **44**, 508 (1910). 36. Jones: J. chim. phys., **9**, 217 (1911). 37. Winston: THIS JOURNAL, **45**, 547 (1911). 38. Wightman and Jones: *Ibid.*, **46**, 56 (1911). 39. Hosford and Jones: *Ibid.*, **46**, 240 (1911). 40. Winston and Jones: *Ibid.*, **46**, 368 (1911). 41. Jones: Carnegie Inst. of Wash., Pub. No. **60** (1907). 42. Jones: *Ibid.*, No. **80** (1907). 43. Jones and Anderson: *Ibid.*, No. **110** (1909). 44. Jones and Strong: *Ibid.*, No. **130** (1910). 45. Jones and Strong: *Ibid.*, No. **160** (1911).

[2] Wied. Ann., **6**, 145 (1879).

EXPERIMENTAL

Preparation of Material.—Kahlbaum's purest salts were used in nearly all cases, and were recrystallized several times from "conductivity water" prepared according to the method of Jones and Mackay.[1]

Apparatus and Method.—The method of Kohlrausch was used, and the apparatus in general has been described by other workers in this laboratory. The bridge was of the Kohlrausch slide wire type, made and standardized by Leeds and Northrup, and graduated in half-millimeters. The cells are described by Clover and Jones[2] and by Jones and West,[3] and the constants were determined every two weeks by means of a 0.02 N solution of potassium chloride, whose conductivity was taken as 129.7. A 0.002 N solution of potassium chloride was used for the cells whose plates were close together, its conductivity having been determined in a cell whose constant had been found by using the 0.02 N solution. Similarly, a 0.0005 N solution of potassium chloride was used to determine the constant for the water cell.

Because of the small conductivity of the water, as compared with that of even the most dilute solutions, a special "water cell" was used which differed from the other cells in having much larger electrodes. These electrodes consisted of two concentric cylinders of platinum from 2.5 to 2.75 inches high, held in position by small pieces of fusible glass, in such a manner that the inner and outer cylinders were a sixteenth of an inch or less apart.

Conductivity measurements were made at 35°, 50° and 65°, at the same dilutions as were used by other workers at the lower temperatures.

Two baths were employed, a smaller one for 35° and 65°, and a larger which was kept at approximately 50° day and night, and carefully adjusted for 50° during the measurements. When the cells were not in use they were kept in the larger bath in order to eliminate such changes in cell constants as

[1] THIS JOURNAL, **19**, 91 (1897).
[2] *Ibid.*, **43**, 192 (1910).
[3] *Ibid.*, **44**, 510 (1910).

would be produced by different temperatures. Each bath was made of galvanized iron, and consisted of two cylindrical vessels which were concentric, with asbestos cement between the vertical walls, and which had a common bottom.

The inner vessel for the smaller bath was 10 inches deep and 12 inches in diameter, while the outer was 10.5 inches deep and 16 inches in diameter. For the larger bath the inner vessel was 14 inches deep and 14 inches in diameter, the outer 14.5 inches deep and 18 inches in diameter.

"Asbestos wood" covers, $^1/_8$ inch thick, treated with a small amount of paraffin, were used on the baths. They were octagonal in shape, just large enough to extend over the rims of the outer vessel of each bath. Two circular holes, 2.25 inches in diameter, were cut in each cover, one in the center for the stirrer and thermometer, the other nearer the edge and over the line of cells supported in the bath. Brass guides were fastened to the edges so that the covers could be rotated upon the rims of the outer vessels.

The covers were cut and hinged so that the larger part was about two-thirds, and the smaller one-third of the whole. In the smaller part was the hole referred to, through which the wires were passed from the coil, etc., to each cell. The hole in the center was covered with a circular piece of asbestos wood, cut in two and fastened together after making small holes in it for the thermometer and stirrer. This did not revolve with the large cover.

Obviously the cover should be so constructed and fitted that as much heat as possible is retained in the bath with minimum evaporation of the water. On the other hand, it was necessary to remove the cells from time to time to inspect them and to eliminate air bubbles. It was also necessary to insert the wires into the cells and to change them to other cells. Thus, the cover must prevent loss of heat, and at the same time the cells must be accessible, and it is believed that these results were satisfactorily attained.[1]

The gutta percha supports used for lower temperatures were

[1] Mr. E. J. Shaeffer and Howard have been carrying on similar work, using the same cells and apparatus. Jointly they devised and constructed the accessories to the bath here described.

found to soften and warp at higher temperatures, and, therefore, supports made entirely of brass were used. Each holder supports three cells and the changes from one bath to another were made three cells at a time. If a bath was to be left at a certain temperature for a considerable time, a mercury thermoregulator was used, but usually a constant temperature was satisfactorily maintained within 0°.1 to 0°.2 by means of two low-form burners, one very small which could be carefully regulated, and the other to bring the bath rapidly to the correct temperature.

The cells were connected with a switch by means of a pair of pliable copper wires (No. 14) two or three feet long, and the switch in turn was connected with the other apparatus by larger wires.

Except for the modifications noted, the work was carried on similarly to that described by earlier workers.

Preparation of Solutions.—A few solutions were made by weighing out the purified salt and adding the correct amount of solvent. In most cases, however, a solution stronger than the strongest to be measured was made up and analyzed, and dilutions prepared from this.

The measuring apparatus was calibrated at 20°. When the "mother solution" was prepared, sufficient salt or salt solution was taken and placed in a measuring flask, and this was kept in the 50° bath for an hour and then water at the same temperature added to the mark. On cooling to 20° this was measured into the different burettes and flasks, and the desired volumes made up. The readings at 35° were multiplied by the factor 0.994 and those at 65° by the factor 1.0076.

Every one of the following results is the average of at least three measurements. A general discussion follows the tables:

Table I.—Sodium Ferrocyanide, $Na_4Fe(CN)_6.12H_2O$

The original solution was made by direct weighing of the anhydrous salt.

Molecular Conductivity

V	35°	50°	65°
8	306.61	386.89	469.609
16	330.29	418.91	508.689
32	380.43	487.25	593.800
128	457.93	594.44	727.678
512	554.43	730.35	909.856
1024	591.86	781.99	979.348
2048	614.64	804.49	1000.842
4096	633.20	803.01	968.996

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	5.35	1.74	5.51	1.42
16	5.89	1.78	5.99	1.43
32	7.12	1.87	7.10	1.46
128	9.10	1.98	8.88	1.49
512	11.73	2.11	11.90	1.63
1024	12.68	2.14	13.16	1.68
2048	12.66	2.06	13.09	1.63
4096	11.33	1.78	11.06	1.38

Percentage Dissociation

V	35°	50°	65°
8	48.42	48.09	46.92
16	52.16	52.07	50.83
32	60.08	60.57	59.33
128	72.32	73.89	72.71
512	87.56	90.78	90.91
1024	93.47	97.20	97.85
2048	97.07	100.00	100.00
4096	100.00	99.82	96.82

Table II.—Potassium Carbonate, K_2CO_3

The original solution was made by direct weighing of the salt after heating for several hours at 110°.

Molecular Conductivity

V	35°	50°	65°
2	158.35	199.34	228.63
8	191.45	237.57	291.17
16	216.87	278.66	341.86
32	228.87	296.51	369.42
128	263.89	340.18	424.50
512	284.36	378.64	468.12
2048	279.17	349.12	423.18
4096	253.01	314.61	376.53

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.73	1.73	1.95	0.98
8	3.07	1.60	2.57	1.08
16	4.12	1.90	4.21	1.51
32	4.51	1.97	4.86	1.64
128	5.09	1.93	5.62	1.32
512	6.29	2.21	5.89	1.26
2048	4.66	1.66	4.94	1.17
4096	4.11	1.62	4.13	1.10

Percentage Dissociation

V	35°	50°	65°
2	55.69	52.65	48.84
8	67.33	62.74	62.20
16	76.26	73.59	73.03
32	80.48	78.31	78.92
128	92.80	89.84	90.68
512	100.00	100.00	100.00
2048	98.17	92.20	90.40
4096	88.97	83.09	80.43

Table III.—Potassium Permanganate, $KMnO_4$

The permanganate solution was standardized volumetrically against potassium tetroxalate.

Molecular Conductivity

V	35°	50°	65°
8	126.75	159.16	193.58
32	136.68	171.71	208.58
128	144.75	181.98	222.22
512	146.39	185.19	226.46
1024	145.39	182.45	215.95
2048	147.12	183.16	215.22
4096	146.26	178.59	205.22

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.16	1.70	2.29	1.44
32	2.32	1.70	2.46	1.43
128	2.48	1.71	2.68	1.47
512	2.59	1.77	2.75	1.48
1024	2.47	1.70	2.23	1.22
2048	2.40	1.63	2.14	1.17
4096	2.16	1.48	1.78	0.997

Percentage Dissociation

V	35°	50°	65°
8	86.15	85.94	85.48
32	92.90	92.72	92.10
128	98.39	98.27	98.13
512	99.50	100.00	100.00
1024	98.82	98.52	95.36
2048	100.00	98.90	95.04
4096	99.42	96.44	90.62

Table IV.—Dipotassium Phosphate, K_2HPO_4

The original solution was standardized by determining the phosphoric acid as magnesium pyrophosphate.

Molecular Conductivity

V	35°	50°	65°
2	139.86	175.07	212.29
8	184.28	234.37	285.21
32	221.75	285.70	350.72
128	252.43	321.93	396.74
512	290.51	346.06	427.15
1024	275.92	347.79	434.00
2048	268.44	344.92	432.97
4096	265.74	340.29	426.20

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.35	1.68	2.48	1.42
8	3.34	1.81	3.39	1.44
32	4.26	1.92	4.33	1.52
128	4.63	1.83	4.32	1.34
512	3.70	1.27	5.41	1.56
1024	4.78	1.73	5.75	1.65
2048	5.09	1.90	5.87	1.70
4096	4.97	1.87	5.73	1.68

Percentage Dissociation

V	35°	50°	65°
2	48.14	50.34	48.91
8	63.43	67.39	65.72
32	76.33	82.15	80.81
128	86.89	92.56	91.42
512	100.00	99.50	98.42
1024	94.98	100.00	100.00
2048	92.40	99.17	99.77
4096	91.48	97.84	98.20

Table V.—Dipotassium Phosphate, K_2HPO_4

These readings were made *one month later* from solutions made up from the same mother solution as those of Table IV.

Molecular Conductivity

V	35°	50°	65°
2	197.54	247.08	298.51
8	315.66	401.01	487.30
32	334.60	427.58	519.59
128	372.53	478.50	590.59
512	414.08	533.40	659.24
1024	426.42	545.14	676.53
2048	422.17	545.44	671.96
4096			

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	3.30	1.66	3.43	1.39
8	5.66	1.79	5.75	1.43
32	6.20	1.85	6.14	1.44
128	7.07	1.90	7.45	1.56
512	7.95	1.92	8.39	1.57
1024	7.91	1.85	8.76	1.61
2048	8.22	1.95	8.43	1.55

Percentage Dissociation

V	35°	50°	65°
2	46.33	45.30	44.12
8	74.02	73.52	72.03
32	78.47	78.39	76.80
128	87.36	87.73	87.30
512	97.11	97.79	97.44
1024	100.00	99.95	100.00
2048	99.00	100.00	99.32

Table VI.—Potassium Sodium Sulphate, $KNaSO_4$

The solution was made by weighing the dry salt.

Molecular Conductivity

V	35°	50°	65°
4	182.65	225.23	272.73
8	199.55	251.17	305.40
32	237.05	301.65	367.39
128	270.35	345.97	424.23
512	291.20	375.47	455.59
1024	297.42	382.60	469.31
2048	307.87	395.50	489.05
4096	330.07	427.44	521.52

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.84	1.55	3.17	1.41
8	3.44	1.72	3.61	1.44
32	4.31	1.82	4.38	1.45
128	5.04	1.86	5.22	1.51
512	5.62	1.93	5.34	1.42
1024	5.68	1.91	5.78	1.51
2048	5.84	1.90	6.24	1.58
4096	6.09	1.85	6.35	1.46

Percentage Dissociation

V	35°	50°	65°
4	55.34	52.69	52.30
8	60.46	58.76	58.56
32	71.82	70.57	70.45
128	81.91	80.94	81.34
512	88.22	87.84	87.36
1024	90.11	89.51	89.99
2048	93.17	92.53	93.77
4096	100.00	100.00	100.00

Table VII.—Potassium Chromium Sulphate (Violet), $KCr(SO_4)_2.12H_2O$

The original solution was standardized by determining the sulphuric acid as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
8	166.97	201.86	242.04
16	183.28	219.21	276.73
32	225.77	271.70	339.90
128	288.11	363.28	467.30
512	404.13	499.67	658.91
1024	465.44	586.07	785.37
2048	546.86	701.81	928.44
4096	637.39	818.02	1082.97

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units.	Per cent.	Cond. units	Per cent.
8	2.33	1.39	2.68	1.33
16	2.39	1.30	3.83	1.28
32	3.06	1.36	4.55	1.67
128	4.34	1.46	6.93	1.91
512	6.37	1.57	10.62	2.15
1024	8.04	1.73	13.29	2.27
2048	10.33	1.89	15.11	2.15
4096	12.04	1.89	17.66	2.16

Percentage Dissociation

V	35°	50°	65°
8	26.20	24.68	22.35
16	28.75	26.80	25.55
32	35.42	33.21	31.39
128	46.77	44.41	43.15
512	63.40	61.08	60.84
1024	73.02	71.65	72.52
2048	85.80	85.79	85.73
4096	100.00	100.00	100.00

Table VIII.—Potassium Chromium Sulphate (Green)

This solution was made by heating the original violet solution at 80° for at least eight hours.

Molecular Conductivity

V	35°	50°	65°
8	193.98	221.47	248.10
16	219.16	252.44	279.35
32	270.38	318.16	352.59
128	357.98	437.81	485.99
512	474.89	618.30	699.33
1024	487.61	658.54	771.94
2048	535.90	753.80	903.28
4096	584.29	848.62	1017.05

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.83	0.94	1.78	0.80
16	2.22	1.01	1.79	0.71
32	3.19	1.18	2.30	0.72
128	5.32	1.49	3.21	0.73
512	9.56	2.01	5.40	0.87
1024	11.39	2.34	7.56	1.15
2048	14.53	2.71	9.97	1.37
4096	17.62	3.02	11.23	1.32

Percentage Dissociation

V	35°	50°	65°
8	33.20	26.10	24.39
16	37.51	29.75	27.47
32	46.27	37.49	34.67
128	61.27	51.59	47.78
512	81.28	72.86	68.76
1024	83.45	77.60	75.90
2048	91.72	88.83	88.81
4096	100.00	100.00	100.00

Table IX.—Potassium Nickel Sulphate, $K_2Ni(SO_4)_2.6H_2O$

The sulphuric acid was determined as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
8	273.53	343.45	407.67
32	349.04	438.23	527.29
128	432.10	547.33	659.73
512	513.77	655.16	798.45
1024	545.16	695.98	850.21
2048	587.40	752.22	927.00
4096	607.93	785.94	960.54

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.66	1.70	4.28	1.25
32	5.95	1.70	5.94	1.36
128	7.68	1.78	7.49	1.37
512	9.43	1.84	9.55	1.46
1024	10.05	1.84	10.28	1.48
2048	10.99	1.87	11.65	1.55
4096	11.87	1.95	11.64	1.48

Percentage Dissociation

V	35°	50°	65°
8	44.99	43.70	42.44
32	57.42	55.76	54.90
128	71.08	68.64	68.68
512	84.51	83.36	83.13
1024	89.68	88.55	88.51
2048	96.62	95.71	96.51
4096	100.00	100.00	100.00

Table X.—Ammonium Chromium Sulphate (Violet), $NH_4Cr(SO_4)_2.12H_2O$

The sulphuric acid was determined as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
8	169.80	204.92	244.97
16	197.87	239.15	288.79
32	228.59	274.46	333.50
128	302.72	369.58	459.09
512	410.17	508.79	648.99
1024	483.10	604.32	754.79
2048	577.37	713.72	897.35
4096	671.17	853.42	1050.26

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.34	1.38	2.67	1.30
16	2.75	1.39	3.31	1.38
32	3.06	1.34	3.94	1.44
128	4.46	1.47	5.90	1.60
512	5.91	1.44	9.35	1.84
1024	8.08	1.67	10.03	1.66
2048	9.09	1.57	12.24	1.71
4096	12.15	1.81	13.12	1.54

Percentage Dissociation

V	35°	50°	65°
8	25.30	24.01	23.32
16	29.48	28.02	27.50
32	34.06	32.16	31.75
128	45.10	43.31	43.71
512	61.11	59.63	61.79
1024	71.98	70.81	71.87
2048	86.02	83.63	85.44
4096	100.00	100.00	100.00

Table XI.—Ammonium Chromium Sulphate (Green)

This solution was made by heating the original violet solution at 80° for at least eight hours.

Molecular Conductivity

V	35°	50°	65°
8	193.98	223.33	250.70
16	229.79	268.08	299.59
32	268.04	316.57	352.20
128	355.62	436.52	489.76
512	446.13	585.31	673.80
1024	492.16	658.87	789.57
2048	537.15	757.75	924.29
4096	589.81	868.79	1061.73

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.96	1.01	1.82	0.81
16	2.55	1.11	2.10	0.78
32	3.24	1.21	2.38	0.75
128	5.39	1.52	3.55	0.81
512	9.28	2.08	5.90	1.01
1024	11.11	2.26	8.71	1.32
2048	14.71	2.74	11.10	1.46
4096	18.60	3.15	12.86	1.48

Percentage Dissociation

V	35°	50°	65°
8	32.89	25.71	23.61
16	38.96	30.86	28.32
32	45.45	36.44	33.17
128	60.29	50.24	46.13
512	75.64	67.37	63.46
1024	83.44	75.84	74.37
2048	91.07	87.22	87.06
4096	100.00	100.00	100.00

Table XII.—Calcium Bromide, $CaBr_2$

The calcium was determined as the oxide by ignition of the oxalate.

Molecular Conductivity

v	35°	50°	65°
2	176.49	219.99	262.05
8	220.47	278.91	339.40
16	233.42	296.41	362.30
32	250.41	318.70	391.68
128	273.47	350.57	431.83
512	288.84	375.49	458.67
1024	300.23	386.64	477.18
2048	303.99	390.98	487.30

Temperature Coefficients

	35°–50°		50°–65°	
v	Cond. units	Per cent.	Cond. units	Per cent.
2	2.90	1.64	2.84	1.30
8	3.90	1.77	4.03	1.44
16	4.20	1.80	4.39	1.48
32	4.55	1.82	4.86	1.52
128	5.14	1.88	5.42	1.55
512	5.77	1.99	5.54	1.48
1024	5.76	1.92	6.03	1.56
2048	5.80	1.91	6.42	1.64

Percentage Dissociation

v	35°	50°	65°
2	58.06	56.27	53.78
8	72.53	71.34	69.65
16	76.79	75.81	74.35
32	82.37	81.51	80.38
128	89.96	89.66	88.62
512	95.02	96.04	94.12
1024	98.76	98.89	97.92
2048	100.00	100.00	100.00

Table XIII.—Calcium Chromate, $CaCrO_4$

The mother solution was standardized by determining the calcium oxide from ignition of the oxalate.

Molecular Conductivity

V	35°	50°	65°
8	128.60	158.03	187.81
16	145.08	180.02	214.73
32	163.29	204.40	243.98
128	207.22	261.25	315.84
512	247.52	315.98	387.01
1024	261.40	332.29	401.22
2048	269.70	344.41	418.31
4096	266.11	340.24	419.18

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units.	Per cent.	Cond. units.	Per cent.
8	1.96	1.52	1.99	1.26
16	2.37	1.63	2.27	1.26
32	2.74	1.68	2.64	1.29
128	3.60	1.74	3.64	1.39
512	4.56	1.84	4.74	1.50
1024	4.73	1.81	4.60	1.38
2048	4.98	1.85	4.93	1.43
4096	4.94	1.86	5.26	1.55

Percentage Dissociation

V	35°	50°	65°
8	47.68	45.88	44.80
16	53.79	52.44	51.23
32	60.55	59.35	58.20
128	76.83	75.85	75.35
512	91.78	91.75	92.33
1024	96.92	96.48	95.72
2048	100.00	100.00	99.79
4096	98.67	98.79	100.00

Table XIV.—Zinc Nitrate, $Zn(NO_3)_2$.

The zinc was determined as zinc oxide.

Molecular Conductivity

V	35°	50°	65°
4	168.65	211.18	258.65
8	188.01	238.25	289.67
32	218.36	280.00	343.09
128	243.53	312.91	384.97
512	260.98	336.48	415.20
1024	267.95	347.35	428.50
2048	276.37	352.62	434.82
4096	281.02	359.97	445.53

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.84	1.68	3.16	1.50
8	3.35	1.78	3.43	1.44
32	4.11	1.88	4.21	1.50
128	4.63	1.90	4.80	1.53
512	5.03	1.93	5.22	1.55
1024	5.29	1.97	5.41	1.56
2048	5.08	1.84	5.48	1.55
4096	5.26	1.87	5.70	1.58

Percentage Dissociation

V	35°	50°	65°
4	60.01	58.67	58.05
8	66.90	66.19	65.02
32	77.70	77.78	77.01
128	86.66	86.93	86.41
512	92.87	93.47	93.19
1024	95.35	96.49	96.18
2048	98.35	97.96	97.60
4096	100.00	100.00	100.00

Table XV.—Zinc Acetate, $Zn(C_2H_3O_2)_2.3H_2O$

The zinc was determined as zinc oxide.

Molecular Conductivity

V	35°	50°	65°
8	77.18	90.46	100.61
32	122.60	149.28	172.86
128	162.36	205.63	243.46
512	188.21	242.85	298.49
1024	190.99	246.67	298.74
2048	198.90	257.81	319.47
4096	198.27	259.11	320.44

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.89	1.15	0.68	0.75
32	1.78	1.45	1.57	1.05
128	2.88	1.77	2.52	1.23
512	3.64	1.93	3.71	1.53
1024	3.71	1.94	3.47	1.41
2048	3.93	1.98	4.11	1.59
4096	4.06	2.05	4.09	1.58

Percentage Dissociation

V	35°	50°	65°
8	38.80	34.91	31.40
32	61.63	57.61	53.94
128	81.63	79.36	75.98
512	94.63	93.72	93.15
1024	96.02	95.20	93.23
2048	100.00	99.50	99.70
4096	99.68	100.00	100.00

Table XVI.—Lead Chloride, $PbCl_2$

The salt was dried and weighed directly.

Molecular Conductivity

V	35°	50°	65°
64	223.16	277.13	331.22
128	251.27	314.89	379.39
512	290.75	370.26	452.75
1024	305.58	387.25	476.90
2048	316.59	412.06	502.84
4096	326.33	416.97	515.18

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	3.60	1.61	3.61	1.30
128	4.24	1.69	4.30	1.37
512	5.30	1.82	5.50	1.49
1024	5.44	1.78	5.98	1.54
2048	6.36	2.01	6.05	1.47
4096	6.04	1.85	6.57	1.58

Percentage Dissociation

V	35°	50°	65°
64	68.39	66.46	64.29
128	77.01	75.52	73.64
512	89.11	88.80	87.88
1024	93.65	92.87	92.57
2048	97.03	98.82	97.60
4096	100.00	100.00	100.00

Table XVII.—Lead Acetate, $Pb(C_2H_3O_2)_2.3H_2O$

The lead was determined as lead sulphate.

Molecular Conductivity

V	35°	50°	65°
4	27.00	34.57	41.42
8	37.98	48.18	58.12
32	66.83	84.36	102.61
128	105.95	132.56	158.54
512	152.89	191.61	228.18
1024	170.98	214.38	255.53
2048	191.50	242.06	289.42
4096	204.87	260.97	315.50

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	0.51	1.89	0.46	1.33
8	0.68	1.79	0.66	1.37
32	1.17	1.75	1.22	1.45
128	1.77	1.67	1.73	1.31
512	2.58	1.69	2.44	1.27
1024	2.89	1.69	2.74	1.28
2048	3.37	1.76	3.16	1.36
4096	3.41	1.66	3.64	1.39

Percentage Dissociation

V	35°	50°	65°
4	13.18	13.25	13.13
8	18.54	18.46	18.42
32	32.62	32.33	32.52
128	51.72	50.80	50.25
512	74.63	73.42	72.32
1024	83.46	82.15	80.99
2048	93.47	92.75	91.73
4096	100.00	100.00	100.00

Table XVIII.—Nickel Acetate, $Ni(C_2H_3O_2)_2$

The nickel was determined as nickel oxide.

Molecular Conductivity

V	35°	50°	65°	
2	47.95	60.45	72.22	Hydrolysis
8	91.99	115.65	138.32	
16	114.02	144.47	171.27	
32	134.85	171.78	206.39	
128	172.52	223.26	272.67	
512	196.30	256.95	316.98	
1024	206.88	270.18	336.46	
2048	212.66	276.44	247.66	

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	0.32	1.73	0.78	1.29
8	1.58	1.72	1.49	1.29
16	2.03	1.78	1.79	1.24
32	2.56	1.90	2.31	1.34
128	3.38	1.96	3.29	1.47
512	4.04	2.06	4.00	1.56
1024	4.22	2.04	4.42	1.64
2048	4.25	2.00	4.73	1.71

Percentage Dissociation

V	35°	50°	65°
2	22.55	21.87	20.77
8	43.26	41.84	39.79
16	53.62	52.26	49.26
32	63.41	62.14	59.37
128	81.12	80.76	78.43
512	92.31	92.95	91.18
1024	97.18	97.74	96.78
2048	100.00	100.00	100.00

Table XIX.—Uranyl Chloride, $UO_2Cl_2.H_2O$

The uranium in the chloride, nitrate, sulphate and acetate was precipitated with ammonia and weighed as the oxide U_3O_8.

Molecular Conductivity

V	35°	50°	65°
4	160.71	198.60	234.14
8	181.31	227.96	272.75
32	217.37	278.17	339.88
128	244.66	316.71	392.84
512	270.65	353.32	445.64
1024	280.77	366.62	470.77
2048	289.83	384.32	487.43
4096	312.88	414.00	527.23

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.53	1.57	2.37	1.19
8	3.11	1.72	2.65	1.16
32	4.05	1.86	4.11	1.48
128	4.80	1.96	5.07	1.60
512	5.51	2.04	6.15	1.74
1024	5.72	2.04	6.94	1.89
2048	6.30	2.17	6.87	1.79
4096	6.74	2.15	7.55	1.82

Percentage Dissociation

V	35°	50°	65°
4	51.36	47.97	44.41
8	57.95	55.06	51.73
32	69.47	67.19	64.47
128	78.20	76.50	74.51
512	86.50	85.34	84.52
1024	89.74	88.56	89.29
2048	92.63	92.83	92.45
4096	100.00	100.00	100.00

Table XX.—Uranyl Nitrate, $UO_2(NO_3)_2.6H_2O$

Molecular Conductivity

V	35°	50°	65°
4	157.89	199.01	245.03
8	177.97	226.59	277.69
32	216.65	279.42	345.77
128	249.88	327.08	406.32
512	285.11	376.95	476.52
1024	304.61	404.71	514.08
2048	318.91	422.85	538.35
4096	349.78	467.92	596.77

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.74	1.74	3.07	1.54
8	3.24	1.82	3.41	1.50
32	4.18	1.93	4.42	1.58
128	5.15	2.06	5.28	1.61
512	6.12	2.15	6.64	1.76
1024	6.67	2.19	7.29	1.80
2048	6.93	2.17	7.70	1.82
4096	7.88	2.25	8.59	1.84

Percentage Dissociation

V	35°	50°	65°
4	45.14	42.53	41.06
8	50.88	48.42	46.53
32	61.94	59.72	57.94
128	71.44	69.90	68.09
512	81.51	80.56	79.85
1024	87.09	86.49	86.14
2048	91.17	90.37	90.21
4096	100.00	100.00	100.00

Table XXI.—Uranyl Sulphate, $UO_2SO_4.3H_2O$

Molecular Conductivity

V	35°	50°	65°
8	158.81	179.79	197.94
32	201.03	223.69	240.24
128	158.21	288.77	309.93
512	333.38	381.83	416.68
1024	377.29	436.95	488.19
2048	428.71	512.04	582.85
4096	484.32	597.28	694.01

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.40	0.88	1.21	0.67
32	1.51	0.75	1.10	0.49
128	2.04	0.79	1.41	0.49
512	3.23	0.97	2.32	0.61
1024	3.97	1.05	3.42	0.78
2048	5.49	1.28	4.72	0.92
4096	7.53	1.55	6.45	1.08

Percentage Dissociation

V	35°	50°	65°
8	32.79	30.10	28.52
32	41.51	37.45	34.62
128	53.31	48.35	44.66
512	68.83	63.93	60.04
1024	77.90	73.16	70.34
2048	88.52	85.73	83.98
4096	100.00	100.00	100.00

Table XXII.—Uranyl Acetate, $UO_2(C_2H_3O_2)_2.2H_2O$

Molecular Conductivity

V	35°	50°	65°
8	50.15	63.14	77.48
32	66.36	82.48	99.33
128	86.21	106.30	126.95
512	109.30	132.66	156.86
1024	119.64	144.10	170.74
2048	131.55	158.30	185.97
4096	151.69	183.60	216.99

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.87	1.73	0.97	1.54
32	1.07	1.61	1.12	1.36
128	1.34	1.55	1.38	1.30
512	1.56	1.42	1.61	1.21
1024	1.63	1.36	1.78	1.23
2048	1.78	1.35	1.84	1.16
4096	2.13	1.40	2.23	1.21

Percentage Dissociation

V	35°	50°	65°
8	33.1	34.4	35.7
32	43.8	44.9	45.8
128	56.8	58.9	58.5
512	72.1	72.3	72.3
1024	79.2	78.5	78.7
2048	86.7	86.2	85.7
4096	100.0	100.0	100.0

Table XXIII.—Hydrochloric Acid, HCl

The original solution, made by passing a calculated amount of hydrogen chloride gas into "conductivity" water, was standardized against a solution of alcoholic potash which had been standardized against potassium tetroxalate (kindly furnished me by Dr. H. O. Eyssell). The results agreed almost exactly with a determination of the chlorine gravimetrically as silver chloride.

Molecular Conductivity

V	35°	50°	65°
8	409.41	479.21	545.15
16	419.19	493.70	562.18
32	430.36	511.38	579.44
128	440.73	522.12	596.58
512	444.27	525.32	598.69
1024	434.68	510.79	585.20

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.65	1.14	4.40	1.92
16	4.97	1.19	4.57	0.93
32	5.40	1.25	4.54	0.89
128	5.43	1.23	4.96	0.95
512	5.43	1.22	4.89	0.93
1024	5.07	1.17	4.96	0.97

Percentage Dissociation

V	35°	50°	65°
8	92.15	91.22	91.06
16	94.35	93.98	93.90
32	96.87	97.35	96.78
128	99.20	99.39	99.65
512	100.00	100.00	100.00
1024	97.84	97.23	97.75

Table XXIV.—Nitric Acid, HNO_3

Standardized against the alcoholic potash which was used for hydrochloric acid (*q. v.*).

V	35°	50°	65°
4	366.32	428.63	472.54
8	386.08	454.51	511.18
16	399.13	466.54	529.08
32	412.37	486.24	553.20
128	421.25	499.17	569.97
512	425.26	503.90	577.82
1024	416.39	493.80	609.91

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	4.15	1.13	2.93	0.68
8	4.56	1.18	3.78	0.83
16	4.49	1.13	4.16	0.89
32	4.92	1.19	4.46	0.92
128	5.19	1.23	4.72	0.95
512	5.24	1.23	4.93	0.98
1024	5.16	1.24	7.74	1.57

Percentage Dissociation

V	35°	50°	65°
4	86.14	85.06	77.48
8	90.79	90.20	83.81
16	93.86	92.59	86.75
32	96.97	96.50	90.70
128	99.06	99.06	93.45
512	100.00	100.00	94.74
1024	97.91	97.99	100.00

Table XXV.—Sulphuric Acid, H_2SO_4

The acid was determined as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
4	377.48	412.68	443.74
8	477.22	527.78	564.55
16	504.21	554.34	597.19
32	551.37	600.95	641.99
128	657.91	718.48	757.05
512	797.94	893.04	953.00
2048	862.33	998.08	1111.85
8192	892.55	1077.34	1203.92

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.35	0.62	2.07	0.50
8	3.37	0.71	2.45	0.46
16	3.34	0.61	2.86	0.52
32	3.31	0.60	2.74	0.46
128	4.04	0.61	2.57	0.36
512	6.34	0.79	4.00	0.45
2048	9.05	1.05	7.58	0.76
8192	12.32	1.17	8.44	0.78

Percentage Dissociation

V	35°	50°	65°
4	42.3	38.3	36.9
8	53.5	50.1	46.9
16	56.5	51.5	49.6
32	61.8	55.8	53.3
128	73.7	66.7	62.9
512	89.4	82.9	79.2
2048	96.6	92.6	92.4
8192	100.0	100.0	100.0

Jones and Caldwell,[1] Jones and MacKay[2] and Jones and Hosford[3] have shown by tables that the value for the molecular conductivity of an alum is less than that of the sum of its constituent salts, and that these differences are little affected by rise in temperature. The tables compiled by

[1] THIS JOURNAL, **25**, 349 (1901).
[2] *Ibid.*, **34**, 357 (1905).
[3] *Ibid.*, **46**, 240 (1911).

Hosford from earlier work done in this laboratory show further that the differences are smaller the greater the dilution. This is what would be expected since dissociation increases with dilution.

The complexities of the changes of the violet chrome alums into green varieties readily account for their irregularities, but there follow tables which show that in addition to ionization, there is a breaking down of the complex salts into simpler ones. The tables are compiled from the work of Drs. Winston[1] [$Cr_2(SO_4)_3$, $(NH_4)_2SO_4$, and Na_2SO_4], West[2] (K_2SO_4) and Hosford[3] ($NiSO_4$):

Table XXVI.—Conductivities of Complex Salts

Ammonium Chromium Sulphate

V	$Cr_2(SO_4)_3$	$(NH_4)_2SO_4$	Sum/2	$NH_4Cr(SO_4)_2$	Diff.
8	151	213	182	170	—12
32	230	255	242	229	—13
128	338	292	315	303	—12
512	472	313	392	410	+18
1024	562	323	442	483	+41
2048	708	337	522	577	+55

Potassium Nickel Sulphate

V	K_2SO_4	$NiSO_4$	Sum	$K_2Ni(SO_4)_2$	Diff.
8	220	93	313	273	—40
32	260	127	387	349	—38
128	297	172	469	432	—37
512	320	219	539	514	—25

Potassium Sodium Sulphate

V	K_2SO_4	Na_2SO_4	Sum/2	$KNaSO_4$	Diff.
8	220	178	199	200	+1.0
32	260	215	237.5	237	—0.5
128	297	247	272	270	—2.0
512	320	270	295	291	—4.0

Potassium Chromium Sulphate

V	$Cr_2(SO_4)_3$	K_2SO_4	Sum/2	$KCr(SO_4)_2$	Diff.
8	151	220	185	167	—18
32	230	260	245	226	—19
128	338	297	317	298	—19
512	472	320	395	404	+ 9

[1] THIS JOURNAL, **46**, 368 (1911).
[2] *Ibid.*, **34**, 357 (1905).
[3] *Loc. cit.*

Hydrolysis was noted in several instances and one salt, dipotassium phosphate, showed a time factor.

Jones and MacKay,[1] in their study of the alums, found that the conductivities for certain of the alums were not constant but changed with time. Some of their results are taken from the paper cited.

Sodium Aluminium Alum

V	Time	Molecular conductivity
20000	0	529
20000	24 hrs.	550

Ammonium Chromium Alum

2000	0	630
2000	24 hrs.	686

Ammonium Iron Alum

200	0	320
200	2 hrs.	330
400	0	411
400	20 min.	424
2000	0 min.	694
2000	30 min.	808
2000	18 hrs.	891
2000	21 hrs.	896

When we made our measurements with dipotassium phosphate they were found not to agree with those of Miss Winston, and were therefore repeated a week later, when it was found that there was still greater disagreement. At about this time some of the cells were sent away for repairs and it was three weeks before the work could again be repeated. The same mother solution was used and, as the next table shows, for concentrated solutions the variation was again increased. The table shows two things. First, the time factor for hydrolysis is greater for concentrated than for dilute solutions. Second, the temperature has little effect on the time factor. According to the law of mass action, the first would be expected. It is, however, undoubtedly true that a cause of the discrepancies between this work and the earlier work is accounted for in the time required for the hydrolysis equilibrium of the salt.

[1] THIS JOURNAL, **19**, 105 (1897).

Table XXVII.—Molecular Conductivities of Dipotassium Phosphate

Column I. Jones and Winston[1]
Column II. From readings made November 22
Column III. From readings made November 28
Column IV. From readings made December 22

	35°			
V	I	II	III	IV
2	138	140	187	198
8	175	184	307	316
32	204	222	332	334
128	230	252		372
512	240	290	420	414
1024	243	276	427	426
2048	243	268	424	422
4096	251	265	424	

	50°			
V	I	II	III	IV
2		175	233	247
8		234	387	401
32		286	422	428
128		322	491	479
512		346	541	533
1024		348	550	545
2048		345	546	545
4096		340	544	

The salts brought within the range of this investigation crystallizing with the largest number of molecules of water are sodium ferrocyanide, $Na_4Fe(CN)_6.12H_2O$, potassium chromium sulphate, $KCr(SO_4)_2.12H_2O$, potassium nickel sulphate, $K_2Ni(SO_4)_2.6H_2O$, and ammonium chromium sulphate, $NH_4Cr(SO_4)_2.12H_2O$. These salts have the largest temperature coefficients of any of those studied, and at the highest dilutions and temperatures vary between eleven and eighteen conductivity units for each degree. Furthermore, for every salt that did not undergo hydrolysis, the temperature coefficients increased with dilution up to infinite dilution, that is, up to that dilution which showed the greatest molecular conductivity.

[1] *Loc. cit.*

When hydrolysis takes place the temperature coefficients do not increase so regularly with dilution, although, in general, these coefficients become larger with increased dilution. These observations agree with those previously published.[1]

Hosford and Jones[2] have shown that while the violet variety of ammonium chrome alum has a smaller conductivity than the green in more concentrated solutions, in the more dilute the green has the smaller conductivity, the change taking place between $V = 1024$ and $V = 2048$. This is true at lower temperatures. At higher temperatures the values for both the green and the violet varieties are more nearly equal, due probably to a gradual transformation of the violet into the green variety (see Jones and MacKay[3]).

Monti,[4] Recoura[5] and Whitney[6] have studied the nature of the transformation of the violet chromium sulphate into the green, and undoubtedly the same changes take place in the presence of ammonium and potassium sulphates, that is, in solutions of the alums.

Whatever the interpretation, there is no doubt that a complex ion is formed, made up of SO_4 and Cr. This does not separate into the chromium or sulphuric acid ions, since ammonia will not precipitate all the chromium nor barium chloride all the sulphuric acid. The measurements show that the sum of the conductivities of this complex ion and such others as may be formed is greater than that for the ions from the violet chromium sulphate or the alum.

After the conductivities of potassium permanganate had been measured the cells were found to have been stained brown with manganese dioxide. As the mother solution had been heated to 50°, undoubtedly there was greater decomposition than would have appeared had the solutions been made up originally at, say, 20°. This will account for the lower values obtained at higher temperatures.

[1] Jones: THIS JOURNAL, **35**, 450 (1906).
[2] *Loc. cit.*
[3] THIS JOURNAL, **19**, 103 (1897).
[4] Z. anorg. Chem., **12**, 75 (1896).
[5] Ann. chim. phys., [7] **4**, 494 (1895).
[6] Z. physik. Chem., **20**, 40 (1896).

The four salts of uranyl that were studied underwent more or less hydrolysis, and therefore agreement was not found with previous workers. Miss Winston[1] observed an increase in percentage dissociation with rise of temperature for uranyl acetate, and attributed the large dissociation to induction. If, as seems possible, there is always a time factor for hydrolysis, this factor would be greater for concentrated than for dilute solutions.

In uranyl acetate the dissociation is greater for higher temperatures only with greater concentrations.

The first table for dipotassium phosphate shows dissociation percentages greater at higher temperatures, but in the second the decrease is seen to be about normal. These measurements, taken, the second a month after the first, show that the greater the interval of time the lower the percentage dissociation. Hence dissociation when measured before hydrolysis is complete does not give concordant results because the more concentrated solutions are less hydrolyzed than the more dilute.

SUMMARY

1. The molecular conductivities have been measured and the temperature coefficients and percentage dissociation calculated for the following salts and acids: Sodium ferrocyanide, potassium carbonate, potassium permanganate, dipotassium phosphate, potassium sodium sulphate, potassium chromium sulphate (violet and green), potassium nickel sulphate, ammonium chromium sulphate (violet and green), calcium bromide, calcium chromate, zinc nitrate, zinc acetate, lead chloride, lead acetate, nickel acetate, uranyl chloride, uranyl nitrate, uranyl sulphate, uranyl acetate, hydrochloric acid, nitric acid and sulphuric acid.

2. Double salts in general have smaller conductivities than the sums of the conductivities of the constituent salts. These differences are little affected by temperature but become less with greater dilution.

3. Certain apparent discrepancies between this work and that of other workers are explained: 1. By hydrolysis with time

[1] *Loc. cit.*

factor. 2. By decomposition such that new substances are formed.

4. The observations of previous workers as to large temperature coefficients for salts that crystallize with large amounts of water were confirmed. For salts that did not undergo hydrolysis the temperature coefficients increased with dilution.

5. The violet varieties of ammonium and potassium chrome alum have smaller conductivities than the green varieties, but the differences become less at higher temperatures.

6. Hydrolysis was noticed in several instances. One salt, dipotassium hydrogen phosphate, had a time factor which extended over days or even weeks.

7. With the exception of uranyl acetate and dipotassium hydrogen phosphate, there was a decrease in percentage dissociation with rise in temperature. After standing four weeks the phosphate acted normally.

CHEMICAL LABORATORY
JOHNS HOPKINS UNIVERSITY
May, 1912

REPORT

THE MOLECULAR THEORY[1]

There are few doctrines which are of as great interest, from the historical point of view, as the molecular theory. Promulgated in ancient times by Leucippus and Democritus, it has, at different times, passed through the most varying stages; it has been considered as certain truth, it has been scorned as a grossly materialistic picture. Leucippus professed the doctrine that matter consists of indivisible and indestructible atoms which move in space. Democritus held the same views. All phenomena depend upon the collision, the contact and the separation of the atoms. They are of different shapes and sizes.

These ideas were violently combatted by the school of idealistic philosophers at Athens, of Plato and Aristotle, afterwards regarded as the great masters of science; as a matter of fact, they enormously impeded by their doctrines, as

[1] One of a series of addresses made at the University of Paris from March 6 to 13, 1911, and published by A. Hermann & Fils; see Book Reviews, THIS JOURNAL, 48, 548

has been observed by Berthelot, the progress of chemistry. Nevertheless, at the beginning of modern times we find in Gassendi, in Descartes and in Newton practically the same ideas as those of Democritus. Modern chemistry had not yet been born. All sorts of shapes, sizes and movements were attributed to the atoms, which persisted only as a rather ingenuous philosophical conception. It was reserved for Dalton to give a chemical bearing to the atomistic doctrine. To him the movement of the atoms was of secondary interest. This physical part of the atomic hypothesis was developed by Daniel Bernouilli in an interesting memoir (in 1738) which contains the nucleus of the kinetic theory of gases. Descartes had already expressed the opinion that heat results from the movement of the corpuscular particles. Bernouilli put forth the same opinion in a more precise manner. According to him, the quantity of heat contained in air is proportional to its elasticity.

But the great period in the development of the atomistic, or, rather, molecular idea came only after the introduction of the mechanical theory of heat in the middle of the last century. The great masters of this theory, Joule, Clausius, Maxwell, derived with marvelous success, by ingenious calculation, a large number of the properties of gases from their movement. Mention must also be made of Waterston, who, in 1845, twelve years before Clausius, gave a detailed theory of the properties of gases, which, however, was forgotten and brought to light by Lord Rayleigh about half a century later.

The authority of the propounders of the theory, so natural and so attractive that it had already suggested itself to the philosophers of antiquity, was so great that the theory was regarded as an integral part of thermodynamics, the superb creation of the immortal Sadi Carnot; it was regarded, then, as the pure truth. On the other hand, chemists were determining the relative positions of the atoms in the molecules and constructing formulas giving, as it were, the whole topography of the molecules. Opponents were not lacking, as, for example, the somewhat fiery genius of Kolbe, but at last the victory became complete and triumphed in the construction of chemical formulas in space by van't Hoff and Le Bel. Still wider became the extent of this theory when van't Hoff proposed the hypothesis, which has since proved so fertile, that dissolved substances possess all the properties of gases, a hypothesis the first traces of which are found developed in a memoir by Gay-Lussac (1839), who, however, did not consider the quantitative side of the question.

Van't Hoff was in fact an atomist, but a very cautious one. He said that he did not wish to connect his hypothesis with that of the movement of the molecules, proposed by the partisans of the kinetic theory of gases. Nevertheless, the physical chemists who accepted his views followed, in general, this natural road, and Boltzmann and van der Waals declared themselves in favor of the kinetic interpretation of the facts brought out by van't Hoff. At this point, a pronounced reaction was felt. In fact, a large number of the properties of matter could be deduced, without recourse to a kinetic representation, by means of the so-called thermodynamic method developed by Willard Gibbs, Helmholtz, Planck, Duhem, and other masters of modern physical theory. The kinetic theory was, in truth, not very easy to manipulate and for this reason lost a great part of its utility. Boltzmann revived it by reducing it to an application of the theory of probabilities, and this theory found an elegant application in the deduction of the laws of radiation.

Nevertheless, chemists were comparatively insensible of this remarkable progress. The theory claimed to be able to calculate the size of the molecules, but the calculation was quite indirect and led to results which differed considerably, varying from two to one hundred trillions of molecules in a gaseous mass of one cubic centimeter at 0° and atmospheric pressure. The most probable number was about twenty trillions (10^{18}). At this period a reaction was felt. Wald, a Czech philosopher and theorist, published a philosophical analysis on the true significance of the laws of Dalton concerning the constant composition and multiple proportions in the composition of chemical products. He expressed the opinion that industrial products have a constant composition because the manufacturers consider constant composition as a sign of purity and consequently treat their products until they show that constancy. The objection that the products of nature also possess, in general, a constant composition was met by the assertion that nature works in about the same way as the manufacturers, especially in the way of recrystallizations.

This idea would probably not have had much success if there had not existed another tendency, which made itself felt at the same period, of purging thermodynamics as much as possible of every trace of accessory hypotheses. A new exposition of the scientific results in this domain was made in accordance with a method which we call that of energetics. The central theorem of this doctrine of energetics, inaugurated by Helm in 1887, is that every quantity of energy is the prod-

uct of two factors, one called intensity (or potential), the other capacity.

Ostwald accepted these ideas, which he chose as the basis of his exposition of thermodynamics (*Treatise on General Chemistry*, Vol. II, Leipzig, 1893). But the greatest sensation was produced by an address made by Ostwald at the meeting of the German naturalists at Lubeck, in 1895, on the "Demolition of Scientific Materialism." A large number of idealistic philosophers and theologians were attracted by the sensational title and hastened to support this movement. Boltzman, on the other hand, wrote a satirical and decisive criticism in the *Annalen der Physik*.

But Ostwald did not surrender so easily. Called to London to make one of the addresses in memory of Faraday, he showed to the astonished audience, who had hoped to learn something on catalytic phenomena, that the laws of Dalton could be explained without the aid of the molecular theory (1904).

At this time, the first investigations on the limit of the electrical charge, already carried out on quite a large scale by Sir J. J. Thomson and his students, Townsend and Wilson, had led to a value of about 3×10^{-10} electrostatic units. Planck, in 1901, had published his important theoretical calculations which led to a value of 4.7×10^{-10} electrostatic units. This agreement was of an entirely different order from that which had been obtained by means of the kinetic theory of gases. This value corresponds to a number $N = 43 \times 10^{18}$ per cc. or $N = 963{,}000 \times 10^{18}$ per gram molecule, which agrees fairly well with the average number of about 20×10^{18} for the number of molecules in a cubic centimeter under normal conditions, as previously found. It is this absolutely independent determination which completely overcame the opposition to the molecular theory. This road, so full of promise, was followed further and you see in the table below the different values which have been found. You will perhaps especially admire the work of Rutherford and Geiger in England and that of Regener in Germany, who counted the number of α particles emitted by a radioactive preparation by counting the number of scintillations which they produced on a zinc sulphide screen. An electrometer gave the corresponding quantity of electricity. The electrical charge of each α particle was, in fact, found to be double that written in the table, which coincides almost absolutely with the theoretical value given by Planck. It was supposed, therefore, that the α particle consists of an atom of helium, carrying two

unit charges like a bivalent ion, such as Ca or Ba; this assertion is quite natural, since helium has a valence of zero and valence generally changes in even numbers; consequently, the unstable ionized helium must have an electrical charge of two units. You see how little the different determinations made during the years 1908 and 1909 vary from the mean, 4.54. It was therefore thought to be absolutely sure that the truth had been found.

		Minimum charge $e \times 10^{10}$	
H. v. Helmholtz, Richarz	1890	1.29	
H. A. Lorentz, C. J. Stoney	1890	1.29–6.1	
J. S. Townsend	1898	1.2–1.5	
R. F. Lattey	(1909)	5	
J. J. Thomson	1898–99	6.5–6.8	(6.0–8.4)
M. Planck	1901	4.69	
E. Bauer, M. Moulin	(1909)	5.55	
J. Nabl	1902	2	
J. J. Thomson	1903	3.4	(3.3–3.5)
H. A. Wilson	1903	3.1	(2.0–4.4)
H. Pellat	1907	2.46–6.9	
K. Przibram	1907	3.8	(1.7–6.2)
R. H. Millikan, L. Begeman	1908	4.03	(3.66–4.37)
E. Rutherford, H. Geiger	1908	4.65	(4.15–5.5)
E. Regener	1908	4.79	
R. Tabor, R. F. Lattey	1909	4.47	(3.13–5.74)
A. Alexeiew, M. Malikow	1909	4.5	(3.0–6.3)
F. Ehrenhaft	1909	4.46–4.68	
G. Moreau	1909	4.3	(4.1–4.8)
M. de Broglie	1909	4.5	
J. Perrin	1909	4.11, 4.05, 4.50	
R. A. Millikan	1910	4.66	
F. Ehrenhaft	1910	0.8–12.4	(Pt)
		0.9–26.7	(Ag)
		0.5–9.6	(Au)
		0.5–28.9	(P)
K. Przibram	1910	3.45	(O)
		4.2	(Air)
		4.15	(HCl)
		4.7	(P)

Fortunately, another method, different from the electrical method, was found. This was the Brownian movement, which, from the investigations of Regnauld, Wiener, Exner, Renard and Gouy, had been found to conform so closely to the sup-

posed movement of the molecules that it was called the molecular Brownian movement. This movement of little particles of the order of magnitude of 0.001 millimeter had been discovered by an English botanist, R. Brown (1827). The study of it was taken up again during the last five years, when the interest in colloidal solutions rose to a high degree, and when the ultramicroscope had been constructed for the observation of small particles which are not visible with the ordinary microscope. The theory of this movement was put forth by Einstein and de Smoluchowski. Svedberg showed that this movement is of the order of magnitude which is demanded by the kinetic theory for molecules of the size of the particles observed.

This discovery made such a great impression on Ostwald that he conceded that, after all, matter is not continuous but divided into distinct particles which correspond to the molecules.

But it was reserved for Perrin[1] to draw extremely important conclusions from a deep study of the properties of these little particles. You are without doubt familiar with that masterly work, carried out with "Gallic elegance," which wins the admiration of every one. The distribution of the particles under the influence of weight—analogous to the increase in the density of the air from the upper to the lower part of the atmosphere—gave him a value of N equal to 70.5×10^{22} for a gram molecule. The Brownian movement itself gave the very nearly equal number 71.5×10^{22} and finally he was able to determine N by means of the rotation of the little particles, using a formula of Einstein's. In this way he found $N = 65 \times 10^{22}$. These three determinations give the value of N which is at present the most trustworthy—and since the recent experiments of Ehrenhaft and Przibram we can congratulate ourselves on having these direct measurements of the movement of the molecules.

There is still another determination in this field which I consider as being of rare importance. We know now, thanks to the work of Perrin, that suspended particles behave in the same way as the kinetic theory requires of gas molecules. The molecules of solutions probably move in an analogous manner, but, as we have just seen, van't Hoff did not wish to connect his theory of dilute solutions with so uncertain a hypothesis. Fortunately, Svedberg has filled in this gap. We know that molecular transformations do not proceed uniformly. This is true also of the emission of α particles.

[1] See articles of Jean Perrin in the *Revue du mois:* La discontinuité de la matière, Vol. **1**, p. 323; Peut-on peser un atome avec précision? Vol. **6**, p. 513

Regener had verified a formula deduced from the theory of probabilities by von Schweidler, who found that the relative variation d (in percentage) from the mean number n per second is inversely proportional to $\sqrt{n}$. Svedberg repeated the determination with a sample of polonium precipitated on a plate of copper and found $d = 42.3$ per cent. instead of 42.8 per cent. calculated according to von Schweidler's formula, n being 0.559 per second.

Then, he reasoned as follows: In a given volume of a solution, the number of molecules of dissolved substance is not constant on account of the molecular movement. De Smoluchowski has given a formula which makes it possible to calculate, in percentage of the mean number, the deviation d_1 due to this cause. If, now, a radioactive salt, such as polonium chloride, is dissolved in water and if the number of α particles produced per second is observed, the observed number must deviate by a certain amount D from the mean number n, and this deviation must be $D = \sqrt{d^2 + d_1^2}$, where d and d_1 are the deviations calculated from the formulas of von Schweidler and de Smoluchowski. He found the following values:

n =	0.476	0.349	0.224	particles per second
$D_{obs.}$ =	55.3	71.5	83.4	per cent.
$D_{calc.}$ =	58.6	68.8	80.5	per cent.
$d_{calc.}$ =	46.4	54.1	67.6	per cent.

The observation was carried out in such a way that a drop of a solution of polonium chloride was placed under a transparent screen covered with zinc sulphide, which was examined under a microscope. The α particles are emitted from a portion of the solution which has a depth of 0.05 millimeter. The drop is much larger and, consequently, the formula of de Smoluchowski is applicable.

The agreement of the calculated numbers D with the observed numbers is very satisfactory. On the other hand, the difference between D and d, which would hold for immobile molecules (fixed on a copper plate, for example), is sufficiently great to permit of concluding with certitude that the dissolved molecules (here probably the ions) move as demanded by the kinetic theory.

From this, it does not seem possible to doubt that the molecular theory, glimpsed by the philosophers of antiquity, by a Leucippus, by a Democritus, hit the truth, at least in its essential parts.

But let us return now to the determination of the minimum

electrical charge. All the measurements made before 1910 are based on the means taken on a large number of particles. Either the movement of a fog consisting of a large number of particles or the total charge of a large number of α particles was measured, or the movement of simple particles was determined in an electrical field and the charge of this particle was calculated. The isolated measurements were then collected into a mean holding for a large number (Ehrenhaft, de Broglie).

Millikan published isolated values for charged drops falling in an electrical field. He found that the charge varied between the wide limits 8.6×10^{-10} and 29.8×10^{-10}. He collected the values into groups; in a first group, the double minimum charge varied from 8.6 to 10.1; in another, the triple charge varied from 13.5 to 14; in a third, the quadruple charge varied from 17.5 to 19.1. The quintuple charges varied from 22.5 to 24.5; the sextuple charge from 26.9 to 28.8. There are evidently certain charges which are more frequent and are multiples of the minimum charge, which he determined to be 4.66×10^{-10}. However, the groups are not very distinct and for this reason Ehrenhaft has very severely criticized the conclusions of Millikan.

These investigations were carried out on a much larger scale by Ehrenhaft and Przibram, at Vienna, who made several thousand experiments. Ehrenhaft found, on excluding those values which were so small that their reality might be doubted, the following numbers for small metallic particles produced by evaporation in the electric arc or for droplets formed in moist air in contact with yellow phosphorus:

For platinum, minimum charge	0.9 to 12.4
silver	0.9 26.7
gold	0.5 9.6
phosphorus	0.5 28.9

There were, therefore, charges very much lower than those calculated from the mean values; the minimum charge of a separate particle may be but one-fifth (0.9×10^{-10}) that (4.5×10^{-10}) which is regarded as the most probable from the earlier measurements. There are all kinds of charges from this minimum up to six times the mean minimum charge.

Ehrenhaft was very much surprised at the results of his measurements, which seemed incompatible with the large number of determinations made before, to which he himself had contributed and which give results agreeing marvelously with the theoretical value 4.69×10^{-10} calculated by Planck. A new difficulty seemed to arise here. Some authors recal-

culated, from new determinations of the radiation constants, Planck's value, which was somewhat higher than the mean experimental value, and found $e = 5.55 \times 10^{-10}$, i. e., 18 per cent. higher. Later, however, it was found that the number given by Planck is correct.

Ehrenhaft then asked his friend, Przibram, who had also previously contributed to the determination of the minimum charge and found a number about 20 per cent. too small, to carry out new measurements on a still larger scale. Przibram performed this work with an extraordinary assiduity. Just for the particles formed in moist air in contact with phosphorus, he made more than a thousand determinations. He found charges varying from about 0.7×10^{-10} to 190×10^{-10}. The frequency of the charges showed maxima and minima. Taking the difference of the charges for two consecutive maxima or minima, he determined the mean minimum charge and found the following values for charged particles, prepared in the manner indicated:

Particles suspended in electrolytic oxygen	$e = 3.45 \times 10^{-10}$
Particles suspended in air through which electrical discharges were passed	$e = 4.7 \times 10^{-10}$
Particles suspended in fogs of hydrochloric acid[1]	$e = 4.15 \times 10^{-10}$
Particles suspended in air, in contact with yellow phosphorus	$e = 4.7 \times 10^{-10}$

It must be acknowledged that the maxima and minima were not equidistant, as is shown by the figures published by Przibram.

A criticism of Ehrenhaft shows that the groups of Millikan are not distinct, but overlap each other, so that the means are quite subjective. Everything seems to show, then, that the minimum value is but a mean. The numbers of Przibram agree very well with those of Perrin, as shown by the table above.

Series of different experiments, carried out at different times with yellow phosphorus, do not give the same value for e; it varies from about 3×10^{-10} to 7×10^{-10}; it is only the mean which gives the number 4.7×10^{-10} and which agrees fairly well with that found by other authors.

The great success obtained by the first determinations of the minimum charge led Planck to develop a theory of radiation, according to which radiant energy is also composed of small equal quantities, which, however, vary with the wave

[1] Charged by means of radium, otherwise this fog is not charged.

length. This theory seems to be confirmed by some experiments of Stark and Ladenburg. Yet Sir J. J. Thomson, with his great authority, has taken a stand against this opinion which, in fact, it is somewhat difficult to admit, and he has given another explanation of the results of Ladenburg. The difficulties in regard to the minimum electrical charge necessarily increase those of introducing the notion of a minimum energy. We must follow with the greatest interest the development of these ideas which are evidently but at their beginning.

What must we now conclude from the large number of experiments in this field? The kinetic theory of gaseous or liquid matter is evidently established beyond doubt. The great masters, Joule, Clausius, Maxwell and Boltzmann, not to mention Leucippus and Democritus, have found a new confirmation of their divinatory power. It has also been possible, it seems, to ascertain that the mean electrical charge of particles and also of ions is constant and about 4.5×10^{-10} electrostatic units. But this seems to be true only for a very large number of particles or ions. The individual charge varies between quite wide limits. Consequently, it seems probable that a molecule of sodium chloride, which consists of quantities of sodium and chlorine charged with equal quantities of electricity of opposite signs, has not the same composition as another molecule of this salt, but that, if we take a large number of these molecules, the mean composition is constant.

Another hypothesis, according to which all the molecules of a salt would have the same composition but some of them charged positively, others negatively, so that the total charge would be zero, is not admissible.

We would, in fact, in this manner come to the conclusion that not only the ions, but the nondissociated salt also, carried the electricity in the electrolyte. The latter transport of electricity would be similar to metallic conductivity. It would be necessary to make a new hypothesis to explain how it is possible that this conduction without electrolysis can never be detected, and this hypothesis would consist in that there is always proportionality between the conductivity due to the ions and that due to the molecules. Such a hypothesis is extremely artificial and must hence be discarded.[1]

[1] In a memoir dated April, 1911, Millikan has subjected the determinations of Ehrenhaft and Przibram to detailed criticism. Millikan finds, for the minimum charge of droplets of oil or of mercury, $e = 4.9 \times 10^{-10}$ electrostatic units. Somewhat later, Perrin (*Compt. rend.*, **152**, 1165) found that the currents produced within the interior of the droplets used introduce into the experiments of Millikan a

Science advances very rapidly in our day. No chapter of physical chemical science can give a better proof of it than the atomistic theory. We might be tempted to conclude from it that our ideas on scientific problems are of extremely little value, since they change from day to day. Nothing could be more erroneous. The theoretical ideas of Dalton were very much superior to those of the philosophers of antiquity. The superiority consisted in the quantitative element of these laws, which could be verified in a very exact manner. In fact, they also serve as the solid foundation of the development of scientific chemistry since his time. The kinetic theory contributed to a very high degree in giving us a simple representation of the heat energy of matter; in physical chemistry it explained the very important law of Avogadro and that of van't Hoff. The determination of the molecular electrical charge and still more the study of the Brownian movement secured the triumph of the kinetic theory against the attacks of the school of energetics. The deep study of the electrical charge of suspended particles seemed to make probable the fact that the chemical law of the constant composition of chemical products is only a statistical law holding for a large number of molecules. In the same way Avogadro's law, according to which the active force of molecules is proportional to the temperature and independent of the composition of the molecules, does not hold for every individual molecule but only as a mean for a large number of molecules.

The last measurements of Millikan, of Perrin and of his students have still further corrected this irregularity; by establishing the constancy of the minimum charge, they have established that of the chemical composition of each individual molecule.[1]

The aspect has varied rapidly lately, but our conception as to the nature of matter has deepened enormously.

Over the kinetic-molecular theory we can write the motto of this superb city, *Fluctuat nec mergitur*. But the fluctuations diminish more and more and the rapid progress becomes more and more continuous and regular.

SVANTE ARRHENIUS

source of error. He, himself, has given the value $\epsilon = 4.24 \times 10^{-10}$ electrostatic units. J. Roux has repeated the experiments of Millikan with droplets of sulphur, which may be considered as being solid, and has found $\epsilon = 4.17 \times 10^{-10}$ (*Loc. cit.*, p. 1168). Finally, Perrin made new determinations by his own methods and found $\epsilon = 4.2 \times 10^{-10}$ electrostatic units. This value must be considered as the most probable (*Compt. rend.*, **152**, 1380 and 1569). According to these new measurements, the minimum charge really seems to be constant.

[1] See the preceding note, p. 546.

OBITUARY

MORRIS LOEB

Morris Loeb, the well known chemist of New York City, died October 8, 1912, at the age of only 49, having been born in Cincinnati May 23, 1863. He was an alumnus of Harvard (class of 1883) and received his Doctor's degree at Berlin in 1887. The following year he spent at the Universities of Heidelberg and Leipzig. On his return to America, he acted as assistant to Prof. Wolcott Gibbs at Newport, Rhode Island, for one year, and from 1889 to 1891 he was docent at Clark University. From 1891 to 1906 he occupied the chair of chemistry at New York University, being made director of the chemical laboratory in 1895.

Dr. Loeb was a man of wealth and many interests, but even after he abandoned his educational work, his love of science did not wane. He was a member of numerous scientific societies and an officer of many of them. He made unstinted use of his talents and wealth in furthering the interests of art and music, in charities and social service work. To him more than any other one man, perhaps, the Chemists' Club of New York owes its present influential position among the chemists of America and its beautiful club house. The entire furnishings of Rumford Hall, of the Priestley Room, of the Library and Museum, were at his expense. In this building he kept a private laboratory and here he loved to spend what little time his numerous activities left him. At the time of his death he was serving his second term as president of the Club, and at a meeting of the Trustees, held Oct. 8, 1912, it was ordered that the following preamble and resolution be filed:

WHEREAS, Morris Loeb, the President of the Club, has been taken from us by death, and

WHEREAS, He was the leading spirit in bringing to fulfilment ambitions and plans that had long been ours, and

WHEREAS, He was always ready to shoulder burdens and to give help, and

WHEREAS, He was a man of order, and of integrity, in mind and heart, sincere in scholarship, living without malice or scorn, speaking no evil, and generous in judgment, and

WHEREAS, We were drawn to him by ties of deep and abiding affection, now, therefore, be it

Resolved, That we make this minute of our poignant grief at his passing, and that we cherish his memory as another of his great gifts to science and to humanity.

ELLWOOD HENDRICK
CLIFFORD RICHARDSON
WALTER E. ROWLEY
Committee

REVIEWS

CONFÉRENCES SUR QUELQUES THÈMES CHOISIS DE LA CHIMIE PURE ET APPLIQUÉE, faites à l'Université de Paris du 6 au 13 mars, 1911, par SVANTE ARRHENIUS, Directeur de l'Institut Nobel scientifique, à Stockholm. Paris: Librairie Scientifique A. Hermann et Fils. 1912. pp. 112. Price, Fr. 3.

The titles of the five lectures contained in this little book are as follows: The Molecular Theory; Suspensions and the Phenomena of Absorption; Free Energy; The Atmospheres of the Planets; The Physical Conditions of the Planet Mars. Anything which Arrhenius has to say is sure to be of interest and this is especially true of the present series of addresses, as they contain brief, but authoritative and lucid summaries of our knowledge on the subjects treated. A translation of the first lecture will be found on p. 536 of THIS JOURNAL.

C. A. R.

THEORETICAL AND PHYSICAL CHEMISTRY. By S. LAWRENCE BIGELOW, PH.D., Professor of General and Physical Chemistry in the University of Michigan. New York: The Century Co. 1912. pp. xiii + 544. Price, $3.

With text-books it is as with living organisms, the fittest survives. However much the author may feel called on to apologize for introducing a new competitor into the field, he will meet few complaints if he succeeds in producing a book which either collects together more scientific facts of a fundamental character than existing books, more aptly summarizes facts already known, throws new and suggestive light on obscure points, or gives a better digested pedagogical presentation of the most essential facts and principles of his subject. The last, at any rate, the present work may well claim to do. Physical chemistry is admittedly as difficult, as it is important, to teach thoroughly to students still in their earlier courses, and this admirable book will be very welcome to those who have found the classical German works too difficult for their purpose, and have not found a work in English which satisfied their requirements of comprehensiveness and simplicity, combined with scientific soundness of treatment. While the

style at times shows evidences of hasty writing, and the choice of colloquially worded summaries as headings of paragraphs may not please all tastes, the author must be admitted to have a thorough comprehension of the limitations of the average student's mind, and of what will fix things in his memory. The subject matter is well chosen, no small thing in itself where the accumulation of detail is so enormous, and important theoretical deductions, mathematical or otherwise, are not neglected; though one misses the clear sequence of one fundamental theoretical principle, as, e. g., the theory of free energy in a well known German work. The style at times seems rather disconnected from sentence to sentence. Recent advances, such as the subject of radioactivity, are well summarized and chapters are given on the theory of inorganic evolution, and the luminiferous ether, etc. Even the theory of relativity comes in for a couple of pages, in this case unfortunately, since the author, in his rather contemptuous dismissal of its claims, betrays the fact that he has entirely failed to grasp what those clains are.

If criticism may be allowed where so much is admirable, the reviewer would suggest that, in a future edition, a little more attention should be given to precision of statement, especially on physical matters. Calories are not "quantity factors" in heat energy (p. 25) comparable to volume in the product pv, but are units of energy itself; the "gravitation constant" (p. 29) usually means the Newtonian constant, something quite different from the acceleration of gravity; on p. 31, line 4, "unit of mass" should be replaced by "gram;" and the statement relative to the kinetic theory of gases (p. 141) that "We may picture this to ourselves and realize that it must be so," etc., will hardly pass for proof of the identity of mean kinetic energy in two systems of molecules in equilibrium, since the same "reasoning" might just as well be applied to the momentum.

B. B. TURNER

SPECTROSCOPY. By E. C. C. BALY, F.R.S., Grant Professor of Inorganic Chemistry in the University of Liverpool, Fellow of University College, London. With 180 Illustrations. New Edition. Textbooks of Physical Chemistry, Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. xiv + 687. Price, 12 s. 6 d.

The first edition of this book appeared in 1905 and gave "typical investigations" of research work from its practical side. The second edition gives "a résumé of the salient points of the more modern work," thus making the book thoroughly up-to-date.

The first two chapters are historical and include a brief de-

scription of the work of Kirchoff, Angström, Rowland and Michelson. The chapters on "The Slit, Prisms and Lenses," "The Complete Prism Spectroscope," "The Prism Spectroscope in Practice," "The Diffraction Grating," and "The Ruled Grating in Practice," have remained practically unchanged in the second edition, only a few pages being added.

Considerable new material has been added to Chapter 8 on "The Extreme Infrared and Ultraviolet Regions of the Spectrum." This includes a description of radiomicrometers, thermopiles, bolometers, the focal isolation of heat waves, etc. As it seems probable that the infrared is an extremely fertile region for research, the author should have treated the infrared in a more detailed and thorough manner. Energy measurements in this region should be made in absolute units and the treatment of this subject should show how this can be done. It seems that our present knowledge of infrared emission and absorption spectra could have been given much more "saliently" than has been done. The ultraviolet is treated more satisfactorily. It does not include any discussion of the ionizing properties of ultraviolet light. To many this would seem proper in a text-book on spectroscopy.

The chapters on "The Application of Interference Methods to Spectroscopy," "The Practical Resolving Power of the Spectroscope," and "The Photography of the Spectrum," have been changed but little. The chapter on "Methods of Illumination" is improperly named as it includes the work of Schuster, Hemsalech, Schenck, Royds, Milner, Mohler, etc., upon the nature of the spark discharge. The chapter does contain many examples of sources of illumination and includes much new material. The chapter on "Phosphorescence and Fluorescence" is very short. It does not describe the very important work that has recently been done by Wood and others on the fluorescence of gases. The treatment of "Absorption Spectra" is necessarily incomplete on account of the enormous amount of uncorrelated material published. The absorption of organic compounds is given considerable space, whereas inorganic compounds are hardly mentioned.

The succeeding chapters are devoted largely to phenomena that have great theoretical importance. Remarkable as has been the development of our knowledge of spectra, yet chapters such as "The Nature of Spectra," "The Zeeman Effect," "Series of Lines in Spectra" and "Changes of Wave Length" have required but little change. The work on the Zeeman effect of absorbing substances at low temperatures, canal rays and the breaking up of fluorescent spectra into series lines should have been emphasized to a greater extent.

On the whole, the book is well written, though it does possess a compilation tone at times. It contains an enormous amount of information for a book of its size and, considering the unorganized nature of our spectroscopic knowledge at present, the author succeeds very well in giving us the more important part of the science. All students of experimental spectroscopy who cannot afford the luxury of owning Kayser's Handbuch should have Baly's Spectroscopy in their library. W. W. STRONG

ÜBER NEUE THERMODYNAMISCHE THEORIEN (Nernstsches Wärmetheorem und Quantenhypothese). Vortrag gehalten am 16. Dezember, 1911, in der Deutschen Chemischen Gesellschaft in Berlin von DR. MAX PLANCK, Professor der theoretischen Physik an der Universität Berlin. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. 34. Price, M. 1.50.

Planck gives a brief sketch of the development of thermodynamics, and then takes up the Nernst theory, which he defines as follows: "The entropy of a condensed, chemically homogeneous substance at absolute zero is zero."

He points out that this principle is not only important from the standpoint of chemically homogeneous substances but also for mixtures and solutions, and here is its important bearing upon chemistry. For details the lecture itself must be read. H. C. J.

DIE ENTDECKUNG DES RADIUMS. Rede gehalten am 11. Dezember, 1911, in Stockholm bei Empfang des Nobelpreises für Chemie, von MME. P. CURIE. Autorisierte deutsche Ausgabe. Mit 5 Abbildungen. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. 28. Price, M. 1.50.

This lecture, as the title implies, discusses the discovery of this remarkable element, but it does more than that. It takes up some of its more important properties and its decomposition products. The decomposition products of thorium and actinium are also considered. H. C. J.

TAFELN ZUM GEBRAUCHE BEI DER BESTIMMUNG VON BRECHUNGSINDICES nach der Methode der konstanten Deviation von 40°. Von J. F. EIJKMAN, Prof. a/d. Univeristät Gröningen. Gröningen: Gebroeders Hoitsema. 1909.

This book of tables has been compiled to facilitate the calculation of the indices of refraction of liquids when the method of constant deviation is employed. In this method the liquid whose refractive index is sought is placed in a hollow glass prism mounted on the table of a spectrometer and the deviation of the incident light is measured. Having determined this angular magnitude and knowing the refracting angle of

the prism, the tables permit the index of refraction of the liquid to be determined with ease. It is hardly probable, however, that the chemist who has occasion to determine the refractive indices of many liquids will resort to the slow and troublesome method involving the use of the spectrometer when several excellent refractometers are on the market. For those who have no refractometer the method and tables of Eijkman will prove of value. FREDERICK H. GETMAN

HIGHER MATHEMATICS FOR CHEMICAL STUDENTS. By J. RIDDICK PARTINGTON, B.Sc., Fellow of Manchester University. With forty-four diagrams. New York: D. Van Nostrand Co. 1912. pp. 272. Price, $2.00.

The idea of a selection of mathematical material for the special needs of chemical students has much to recommend it, and has already been embodied in some excellent works, both in German (e. g., Nernst and Schoenfliess) and English (Miller). The proper medium between shallow superficiality and a mathematical rigor impossible of attainment by the average student of what is still largely a descriptive science is not easy to hit. The present work seems to be little but a series of selections from ordinary mathematical treatises with a few examples and illustrations from chemistry thrown in. For the unmathematically minded it is neither simple enough in its pedagogy nor suggestive enough of the real importance to him of a clear grasp of a few principles; the student who has sufficient aptitude to work through this book would get much the same results from his college courses in mathematics. B. B. TURNER

A CONCISE HISTORY OF CHEMISTRY. By T. P. HILDITCH. New York: D. Van Nostrand Co. 1911. pp. 250. Price, $1.25.

It is a familiar practice of examiners to ask the well-primed student to state *all that he knows* of (e. g.) the atomic theory—in twenty minutes. Just such breathless haste inspires the pages of this little book, in praise of which it must be admitted that the amount of facts, names, and dates compressed into its 85,000 or 90,000 words is quite amazing. As a history, in the sense of a work which might be put into the hands of the average thoughtful student to give him a clear connected idea of the development of chemical science, it can scarcely be recommended; twice the number of words on one-half the material would have given better results. But as a kind of pocket dictionary of the subject, to which the fully developed chemist may refer, not only for a date, but for very useful tables and pithy explanatory paragraphs, it is well worth buying. While it appears that the desire to "cram" for ex-

aminations was the leading object in compiling this work, it cannot be denied that its author shows judgment as well as remarkably wide reading in his choice of material, and has put the facts into suggestive condensations. The short tables of prominent living workers at the end of the book will help the student in his original reading. It is concise, but hardly history.

B. B. TURNER

THE CHEMICAL CONSTITUTION OF THE PROTEINS. By R. H. A. PLIMMER, D.Sc., Assistant Professor of Physiological Chemistry in, and Fellow of University College, London. In Two Parts, with Diagrams. Second Edition. Part I, Analysis. Monographs on Biochemistry, edited by R. H. A. PLIMMER, D.Sc., and F. G. HOPKINS, M.A., M.B., D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. xii + 188. Price, 5s. 6 d.

The first edition of this monograph is so well and favorably known as to make unnecessary any comment on its general excellence. The second edition shows thorough revision and considerable enlargement over the first. The discussions, both of the hydrolysis of proteins and isolation and estimation of the resulting amino acids, and of the chemical constitution of these amino acids, are thorough in themselves and are supplemented by exceptionally complete bibliographies. The value of the work is still further enhanced by the inclusion of a very complete compilation of the analyses of products of hydrolysis of the various individual proteins, which has been brought so closely down to date as to include data published in 1911.

H. C. SHERMAN

THE PHYSIOLOGY OF PROTEIN METABOLISM. By E. P. CATHCART, M.D., D.Sc., Grieve Lecturer on Chemical Physiology in the University of Glasgow, Research Associate of the Carnegie Institution, Washington. Monographs on Biochemistry, edited by R. H. A. PLIMMER, D.Sc., and F. G. HOPKINS, M.A., M.B., D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 142. Price, $1.25.

This volume, according to the author's preface, does not pretend to cover the whole literature of protein metabolism, but "consists rather of the discussion of the more important results published during the last decade and their bearing upon the work of the earlier investigators." The principal contents are: Digestion and Absorption of Proteins; Protein Regeneration; Feeding Experiments with Abiuret Products of Digestion; Deaminization; Influence of the Food on the Composition of the Tissues; Protein Requirements; Theories of Protein Metabolism; Starvation; Work; and a Bibliography of over 400 titles.

The book is, in the main, clearly and interestingly written

and the material included is generally well digested and concisely presented.

On the other hand, it is surprising to see the work of Chittenden so inadequately presented, and to find discussions of the influence of muscular work on metabolism and of the protein-sparing action of carbohydrate and fat which do not mention the work of Atwater and Benedict on these problems, nor take cognizance of their important findings. Two of the most interesting sections of the book, dealing respectively with the influence of a diet of pure foodstuffs and with the fate of nitrogenous food after absorption, would be much modified by the results recently published by Osborne and Mendel and by Folin and Denis, respectively, which are mentioned only in short footnotes evidently added while the work was in press. Notwithstanding these omissions, the book will doubtless be very useful in bringing before the general worker, in nutrition or food chemistry, an interesting presentation of modern viewpoints, and in furnishing the special student with a convenient summary and selected bibliography of most of the more important literature to the end of 1910. H. C. SHERMAN

ANNUAL TABLES OF CONSTANTS.

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